Chemical Engineering Journal 159 (2010) 272–279

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Short communication

Neural network and principal component analysis for modeling of hydrogen adsorption isotherms on KOH activated pitch-based carbons containing different heteroatoms

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ARTICLE INFO

Article history:
Received 20 December 2009
Received in revised form 26 January 2010
Accepted 27 January 2010

Keywords:
Hydrogen
Adsorption
Pitch-based carbons
Isotherm
Artificial neural network
Principle components
Percent deviation

ABSTRACT

A three-layer feed-forward artificial neural network (ANN) was constructed and tested to model the equilibrium data of hydrogen onto activated carbons containing different heteroatoms. The properties of the activated carbons and the experimental conditions are used as inputs to predict the corresponding hydrogen uptake at equilibrium conditions. The statistical validity of activated carbon properties in discriminating the adsorbent type was carefully studied and validated. The constructed ANN was also found to be precise in modeling the hydrogen adsorption isotherms for all inputs during the training process. The trained network successfully simulates the hydrogen sorption isotherm for the new inputs, which are kept unaware of the neural network during the training process, thus showing its applicability to determine the sorption isotherms for any operating conditions under the studied limits. The absolute percentage deviation between the experimental and predicted data during the training and testing process was observed to be less than 5% for most of the input conditions.

1. Introduction

Hydrogen energy is considered to be an alternative for fossil fuels as it is clean, it can be easily produced, it has high heating value and it is environmentally benign because its oxidation product is water. The storage of hydrogen is a key issue especially in on-board hydrogen storage when used on hydrogen based fuel cells [1]. Reversible adsorption of hydrogen onto carbonaceous materials has been attracting much interest which could be realized from the stimulating studies reporting on the hydrogen adsorption behavior of carbon nanotubes, carbon, graphite fibres, carbon template, activated carbon, etc. [2–5]. Previous studies by several researchers show that the storage capacity of these materials is greatly influenced by the surface area, pore volume and pore size distribution. To enhance the low hydrogen uptake at room temperature by physical adsorption several treatment methods including the deposition of metallic compounds onto activated carbon surface have been reported aiming to increase the hydrogen storage [4,6–8]. Deposition of metals and semi-metals can catalyze or inhibit the reactions taking place during the pyrolysis and may modify the structure of precursors and consequently the adsorptive properties of the activated carbon. The storage capacity of these materials is usually modeled or measured from the widely used theoretical adsorption isotherms, which include Langmuir [9], Freundlich [9,10], Dubinin–Raduskevich [11], Sips [12] and Toth isotherms [9]. The effect of adsorbent properties on the storage capacities is usually modeled with simple linear expressions. A linear empirical expression of type $y = mx + c$ has been widely used to correlate micropore volume, volume of narrow micropores and BET surface area with adsorption capacity at specific operating conditions (pressure or temperature). A linear relationship between methane storage capacity and surface area of different materials was reported by Sun et al. [13] for the adsorption at 3.5 MPa and 298 K. Likewise, a linear relationship was observed between the adsorption capacity for hydrogen and the specific surface area of adsorbents made of different materials [14]. The same authors reported a linear expression based on a plot of hydrogen adsorption capacity versus micropore and mesopore volumes [14].

The activated carbons containing the heteroatom and the reference material reported in this study exhibit a linear relation between total microporosity and narrow microporosity values [4]. Theoretical models can be successfully used to model or to represent the equilibrium uptake of hydrogen at a constant temperature and a range of pressure conditions. Likewise the linear empirical expressions can be useful while representing the effect of any one of the adsorbent property (e.g. micropore volume) with the the-

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doi:10.1016/j.cej.2010.01.059

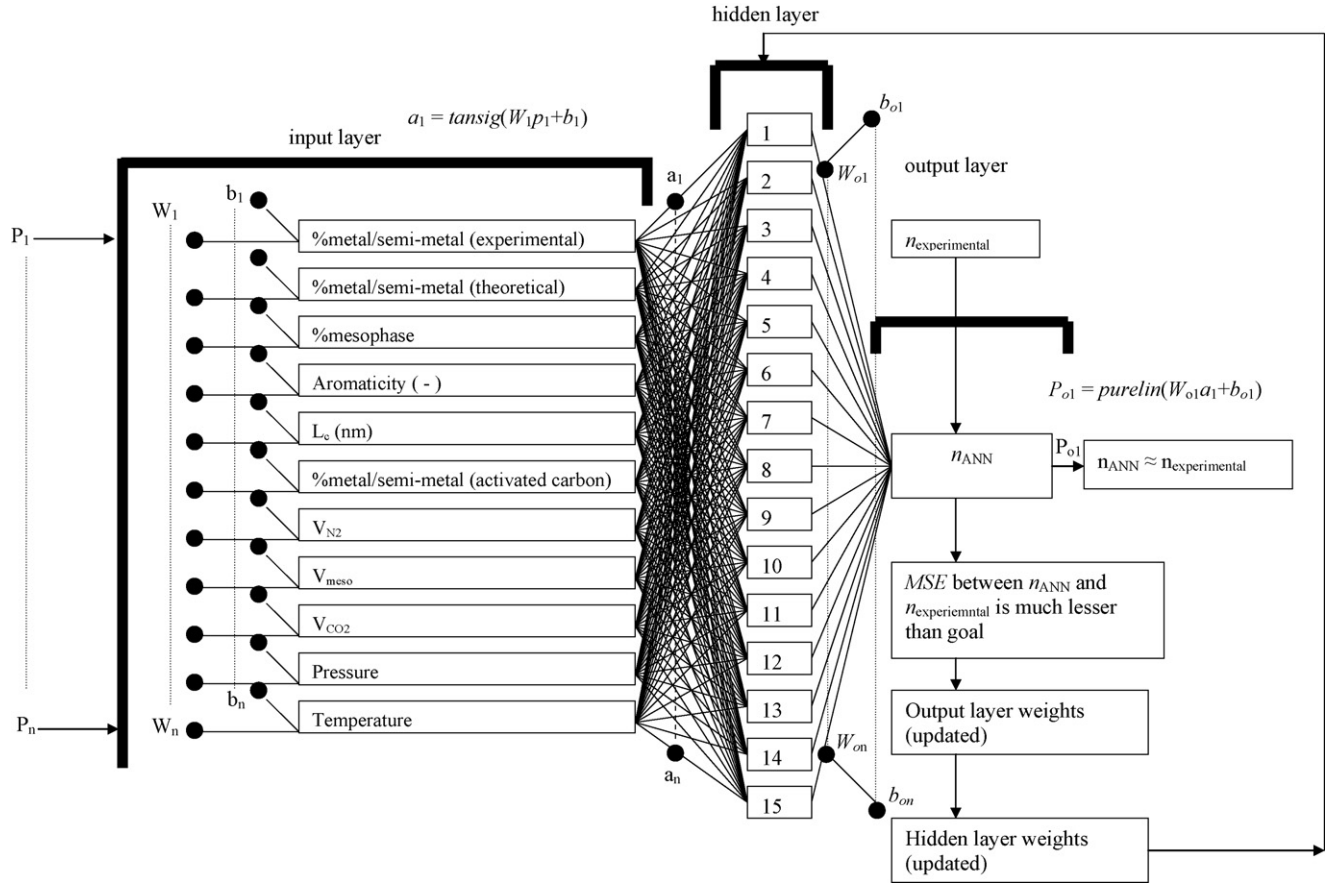

Fig. 1. Structure of the constructed three-layer back propagation network and training strategy of the constructed feed-forward artificial neural network.

oretical sorption capacity of adsorbent. Any attempt to propose a correlation between the hydrogen storage capacity for a wide range of pressures, temperature and adsorbent properties would be a difficult task using theoretical or empirical expressions.

Artificial neural networks (ANNs) could be an option for solving this type of complex problem since they were found to be an excellent option for solving many complex issues. ANN consists of three layers: an input layer (containing input nodes), an output layer (containing output nodes) and a hidden layer (containing hidden nodes). The new information is fed into the network via input nodes. The activities of input nodes along with the weights on links between input and hidden nodes determine outputs of hidden nodes. ANN consists of an input layer and an output layer interconnected by several nodes. ANN can rapidly process a large amount of information and have excellent generalization capability for noisy or incomplete data. ANN models are flexible and well-trained ANN can perform well, where empirical modeling is suitable [15]. In chemical engineering, neural networks was successfully applied to predict the adsorption equilibrium and kinetics of solid/liquid systems [16,17], interfacial tension at crystal/solution interface [18], adsorption of Pb(II) onto *Antep pistachio* [19], leachate flow-rate in a municipal solid waste landfill site [20], prediction of SO_2 concentrations in a metropolitan area [21], estimating the water content of natural gas [22], solubility of proteins [23], kinetics of photocatalytic water treatment [24], etc. To our knowledge, no studies have been reported so far reporting the applicability of artificial neural networks in predicting the adsorption isotherm of hydrogen onto activated carbon containing different heteroatoms. ANNs are used to correlate the complex relationship between the input and output of any process irrespective of the physical meaning of the system. ANN consists of input and output layers connected by several nodes. In the present study a feed-forward or back propagation network with multiple layers was constructed to model the adsorption equilibrium of hydrogen onto an activated carbon containing different heteroatoms for different operating conditions. The constructed network was tested with the new data which are kept unaware of the neural network in order to check the applicability of the network in predicting the hydrogen uptake at equilibrium condition for new experimental conditions.

2. Methods

2.1. Pitch-based activated carbons

An aromatic petroleum residue (ethylene tar-R1) [25,26] was mixed, individually, with four different compounds, triphenylsilane (TPS), pyridine borane complex (PyB), tetrabutyl orthotitanate (TBO) and ferrocene (FC) in an ultrasonic bath for an hour, to give mixtures containing 2 wt.% of Si, Fe and Ti or 1 wt.% of B. All compounds are apparently soluble in the petroleum residue. Pyrolysis of the mixtures was performed at 440 °C, soak time of 4 h and 1 MPa pressure, thus leading to pitches which contain the metal/semi-metal: PSi, PB, PTi and PFe. A reference pitch P was also prepared. The activated carbons PA, PSiA, PBA, PTiA and PFeA have been prepared from the respective petroleum pitches as follows: KOH and the pitch were mixed in a ball mill during 30 min with a impregnation ratio of KOH/carbon of 3/1 and then thermally treated in a horizontal furnace at 800 °C under nitrogen flow of 100 ml/min, soak time of 2 h. Finally, the activated carbon was washed in a Soxhlet apparatus for 24 h with water and dried at 110 °C for 24 h in a vacuum stove.

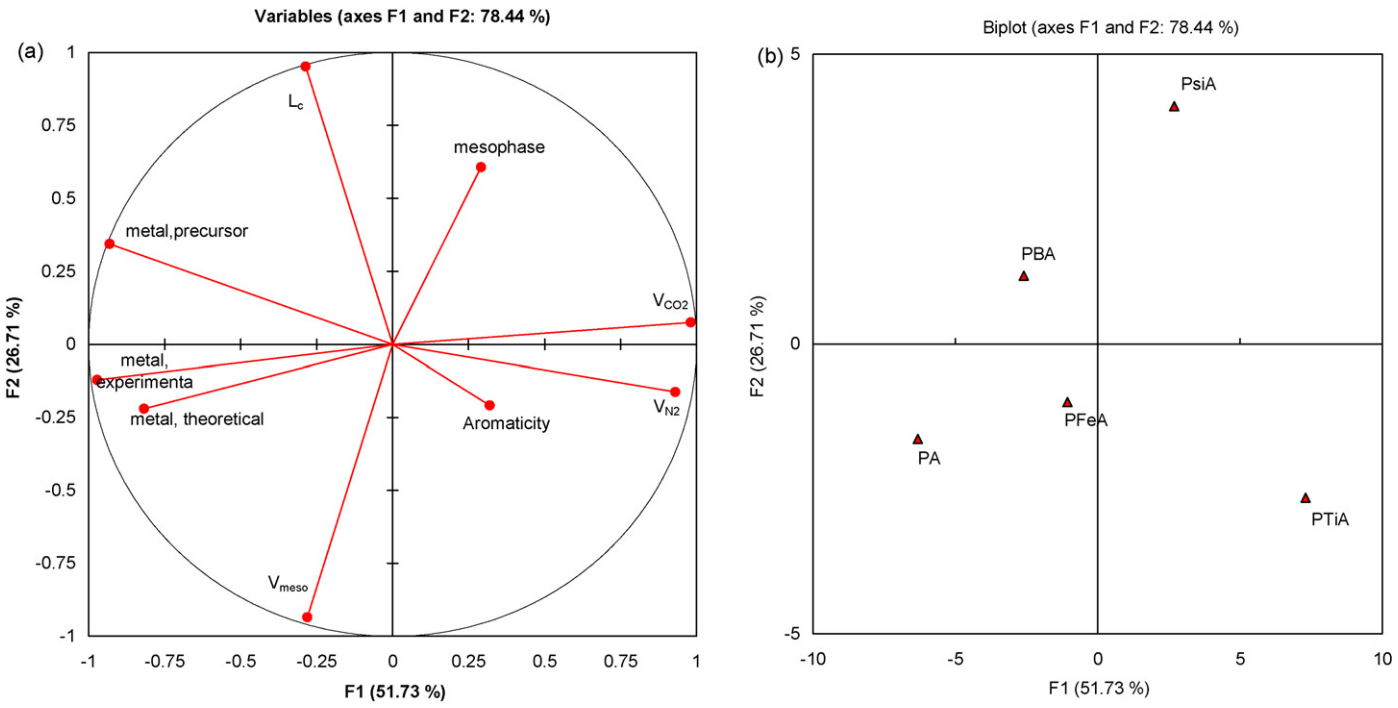

Fig. 2. (a) Correlation circle showing the discrimination power of activated carbon properties. (b) Biplot discrimination of activated carbons containing metals.

2.2. Equilibrium data and network inputs

The hydrogen adsorption isotherms for the pitch-based carbons containing Si, B, Ti and Fe were obtained from the adsorption experiments carried out using a homemade automatic volumetric equipment, which features two pressure transducers covering the pressure ranges 0–0.1 MPa and 0–10 MPa, respectively.

The characteristics of the prepared activated carbons which include: () the % heteroatom content, pore volumes V_{N_2}, V_{meso}, and V_{CO_2} and (i) the characteristics of the pitches which include % heteroatom content (experimental), % metal/semi-metal content (theoretical), % mesophase, aromaticity and the apparent height of the stack (L_c) of mesophase are used as inputs, in addition to the temperature and pressure conditions. The terms V_{N_2}, V_{meso}, and V_{CO_2} refer to the total volume of micropores less than 2 nm, volume of mesopores and the volume of narrow micropores less than 0.7 nm, respectively [27]. The techniques used and characterization results are discussed elsewhere [4].

3. Neural network modeling

In the present study a feed-forward network with three layers was constructed to model and simulate the adsorption isotherms of hydrogen onto pitch-based carbons containing different heteroatoms. Multiple layer networks can approximate any function very well for the given inputs. Feed-forward ANN allows the information signals to flow only in one direction, i.e., from input to output and adjusts the transfer function that is associated with the inputs and outputs. In the present study, a network with one neuron in the hidden layer was constructed initially and trained to simulate the hydrogen sorption isotherms for different input conditions. The detailed structure of the network and the training strategy of the constructed neural network are given in Fig. 1. Fig. 1 shows the feed-forward network with one hidden layer. P_1 is the input vector to the hidden layer, W_1 and b_1 represent the weight and bias of the hidden layer. The information from the hidden layer is transferred to the output layer, as shown in Fig. 1. The term P_2 represents the output vector and can be determined from the weight, W_2 and bias b_2 of the output layer. In the present study a *tansig* and a *purelin* functions were used as the propagation functions in the hidden layer and in the output layer, respectively. The training strategy of the network is shown in Fig. 1, where the input vectors and the corresponding output vectors are used to train the network until it approximates the propagation function. Thus, the bias and the weights can be obtained from the training procedure, which is based on the experimental data. In the present study, the data corresponds to the adsorption isotherms on five pitch-based carbons, on four of which a chemical compound was dissolved that can catalyze or inhibit the reactions taking place during the pyrolysis and thus modify the structure of pitch and, consequently, the adsorptive properties of the activated carbon. Thus considering these issues, the difference in the properties of the pitch-based activated carbons and the properties of pitches in which the chemical compounds were dissolved are included as input parameters while constructing the neural networks.

Selection of input variables is a critical part of neural network design. It is possible to use a combination of own knowledge of the problem domain, and standard statistical tests to make some selection of variables before starting to use neural networks. Alternatively, various combinations of inputs could be tried by experimentally adding and removing input vectors, building new networks for each [19,28] or this could be made by a sensitivity analysis [28]. In this study, the main objective is to make a correlation of the properties of adsorbents and the experimental conditions with equilibrium hydrogen storage using neural networks as this type model cannot be generated using a simple regression analysis. Thus, in this study the physicochemical properties of the activated carbons and the experimental conditions, pressure and temperature are assumed to be the input vectors. The main objective of the manuscript is to provide a model using neural networks to predict the equilibrium hydrogen uptake on activated carbons differing in physicochemical properties as a function of temperature and pressure. In this study, the heteroatom loading (actual and theoretical), mesophase content, aromaticity,

stack height of mesophase molecules and mesogens of the precursor and the metal or semi-metal loading, V_{N_2}, V_{meso} and V_{CO_2} of the prepared activated carbons are used as input vectors. The experimental conditions, temperature and pressure and the corresponding equilibrium uptake of hydrogen onto the carbon particles was defined as the output vector while training the neural network. The significance of the physicochemical properties in representing the adsorbent type was confirmed using a discriminant function analysis which will be discussed in the later sections.

The ability of the input vectors which are used to represent the adsorbent type was analyzed by running a discriminant analysis. Discriminant analysis was performed using a trial version of XLstat, a freely available software. The correlation circle showing the discrimination power of the inputs used in representing the adsorbent type is shown in Fig. 2a. Fig. 2a shows that the first two main components, f_1 and f_2, enable to represent 78% of the total variability of the observed habits (Fig. 2a). The correlation circle, where the position of each descriptor is f_1–f_2 space is plotted, reveals that each descriptor brings significant information, as all of them are well distributed in the circle. Fig. 2b shows that the property of the adsorbent material was also capable to discriminate the adsorbent material based on their sorption capacities. Fig. 2b shows that the adsorbents with relatively higher sorption capacities are on the left side of the graph and adsorbents with poor sorption capacities are on the right side. The sorption capacities of these adsorbents at 77 K and 298 K, as described elsewhere [4], in decreasing order is PBA > PA > PFeA > PSiA > PTiA and PFeA > PA > PBA > PSiA > PTiA, respectively. The observations in Fig. 2a and b indicate that, the characteristic properties of the activated carbon and the precursor are equally important to represent the adsorbent type.

The neural network toolbox Version 4 of MATLAB, Mathworks Inc., was used for simulation. The input and the target vectors were normalized before training to fall in the interval from 0 to 1 so that the mean and the standard deviation are 0 and 1, respectively. The input conditions and the corresponding experimentally determined equilibrium hydrogen uptake concentrations were set as the input and the target vectors. The neural network was trained in a batch mode using a Levenberg–Marquardt's algorithm strategy, which is sensitive to the number of neurons in the hidden layer. The larger the number of neurons, the better is the performance of the neural network in fitting the data. However, a larger number of neurons in the hidden layer will sometimes result in overfitting and to avoid this a Bayesian regularization technique in combination with the Levenberg–Marquardt's strategy was adopted to train the network. The Bayesian algorithm works better when the network input and output are scaled within range of −1 to +1 [29]. In the hidden layer, three types of transfer function, the exponential sigmoid, tangent sigmoid and linear functions were tested initially while training the neural network. The linear function was used at the output layer. A tangent sigmoid function in the hidden layer and a linear function at the output layer was found to be excellent in predicting the hydrogen sorption isotherms of pitch-based carbons containing different metals and physicochemical properties, irrespective of the input conditions.

In this study, the network was trained initially with a Bayesian regularization process as this type of training could eliminate the guesswork necessary to determine the effective number of parameters while optimizing the network. Unfortunately, irrespective of the several input combinations tried during the training process, the network failed to converge while adopting a Bayesian regularization procedure for the range of input conditions. The Bayesian regularization worked better only when the temperature and pressure are used as input vectors. However this network cannot serve the purpose of the objective, as the network does not consider the characteristic properties of the different activated carbons studied. To solve these problems, the network was trained using a Levenberg–Marquardt strategy and regularized using a *userstop* facility available in Matlab. The training process was stopped by *userstop* when the sum of the squared errors, the sum squared weights and the effective number of parameters (weights and biases) are converging to a constant value.

As mentioned earlier, training by Levenberg–Marquart's strategy is subjected to the problems of overfitting and overtraining. Overfitting occurs when too many neurons are in the hidden layer and it can be estimated by the large error deviations between the experimental and the ANN predicted hydrogen adsorption isotherms for the new input data [30]. Overfitting refers to exceeding the optimal size of the neural networks, which may reduce the performance of neural networks in predicting the targets. Overtraining refers to the training time of neural network that will reduce the performance of neural networks [30]. Overtraining of an optimized network will sometimes lead to poor prediction of the targets, as the network will memorize the training examples, but it does not generalize to the new experimental conditions. Thus, the network should be optimized to determine the effective number of parameters and the training time to improve the robustness of the neural network model. Thus, several trials were made using Levenberg–Marquardt's strategy while training the network. A cross-validation approach with one testing set was used in parallel while training the neural network. The neural network was trained and tested in parallel for different number of neurons in the hidden layer for the given input conditions. The network was trained for 123 experimental conditions and was cross-validated for 69 experimental conditions in the training and testing set, respectively. The trained network was also validated with 52 input conditions in a second validation set, which will be discussed later. Thus in total, the network was trained with 123 experimental conditions and validated with 131 new inputs during the testing process. In this study, the network structure was varied starting with one neuron in the hidden layer and, after several trials, the ANN with 15 neurons in the hidden layer was found to be successful in predicting the targets both in the training and testing set.

In this study, the problem of overfitting was eliminated by adapting the cross-validation technique. For cross-validation, a testing set (first validation set) that contains new input conditions that are not used during the training process was used. The problem of overtraining was avoided by using *userstop* while training the neural network. Fig. 3a shows the plot for the mean squared error between the experimental data in the first validation set and the amount adsorbed predicted by the trained neural network and the number of neurons in the hidden layer.

Fig. 3a also shows the plot of number of epochs due to *userstop* while training the neural networks and it can be deduced that the neural network with 15 neurons in the hidden layer performs well in predicting the targets for the new inputs in the first validation set. The mean squared error between the experimental hydrogen uptake and the neural network predicted values for the new inputs in the first validation set was determined to be 2.63×10^{-4} for $N_H = 15$, where N_H represents the number of neurons in the hidden layer.

In all cases the neural network adequately predicted the targets in the training set. Fig. 3a shows that increasing the neurons >15 in hidden layer affect the performance of the neural network in predicting the targets for the inputs in the first validation set. Though the *MSE* between the experimental and *ANN* predicted isotherms (Fig. 3a) are nearly the same for $N_H = 12$ and 15, the performance of network was relatively poor for the inputs in training set when N_H was set to 12 (not shown). Thus, the network with 15 neurons was considered to be an optimum network structure in predicting the targets the range of input conditions studied. The network failed to converge when the number of neurons in the hidden layer

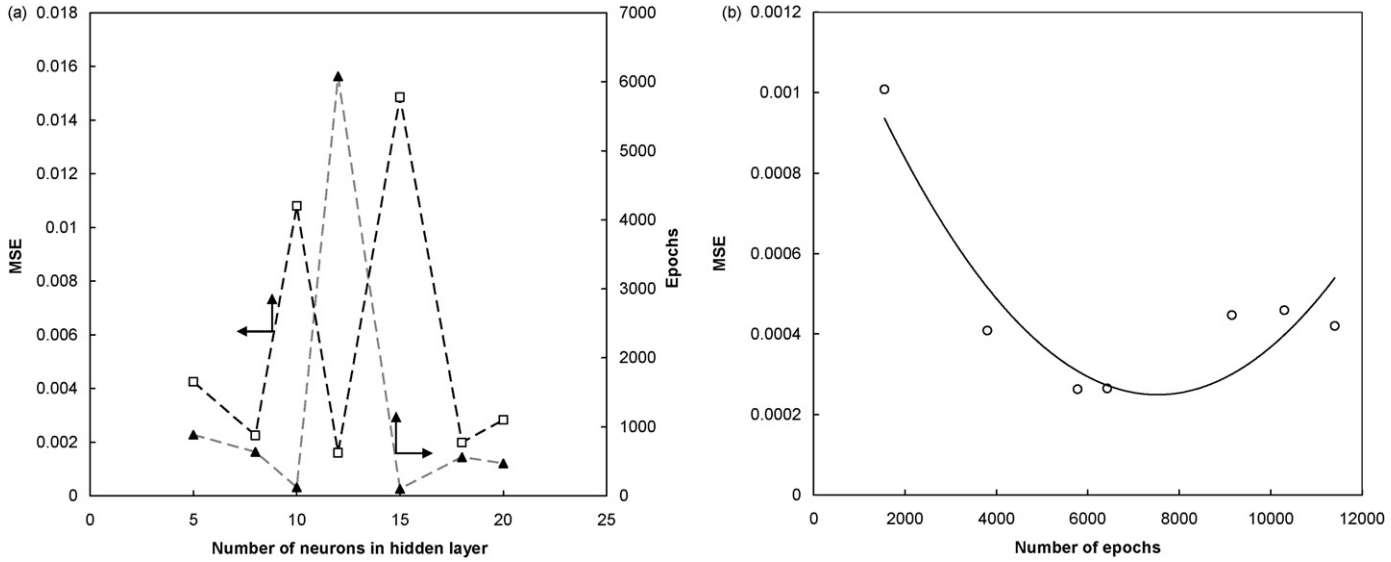

Fig. 3. (a) Mean squared error between experimental and neural network predicted equilibrium data as a function of number of neurons in the hidden layer. (b) Mean squared error between experimental and neural network predicted equilibrium data as a function of training epochs for hydrogen sorption isotherm data onto pitch-based carbons.

was less than or equal to four. The best performance of neural networks in predicting the targets for the new inputs in validation set confirms that there is no overfitting. Fig. 3b shows the plot between number of epochs versus *MSE* between the experimental and the *ANN* predicted hydrogen sorption isotherms. Fig. 3b corresponds to the performance of network for $N_H = 15$, where it can be observed that the network was overtrained for epochs >5776. All values in Fig. 3b were obtained by *userstop* with the initial number of epochs set to 30,000 during the training process. The MSE for the training epochs <5000 are not shown as the visual observation of the training plot at this condition showed that MSE was gradually decreasing at this conditions. Stopping the training process using *userstop* at this condition may lead to results obtained from a network which is not completely trained. The details of the completely trained neural network used in the present study to model and simulate the adsorption isotherms of hydrogen on pitch-based carbons containing different metals are given in Table 1.

Fig. 4 shows the plot between the n_{exp} and n_{ANN} values for the studied carbon adsorbents. n_{exp} and n_{ANN} refers to the experimental and neural network predicted values for the sorption of hydrogen onto carbon materials at equilibrium conditions. It can be observed in Fig. 4 that the developed neural network was excellent in representing the equilibrium data, irrespective of the different properties of carbon materials during the training process. The accuracy of the constructed neural network was verified from the percent deviation between the experimental and predicted isotherms for the carbon materials.

Table 1
Details of trained artificial neural network for the storage of hydrogen onto pitch-based activated carbons containing different metals.

Type	Value/comment
Input layer	11
Hidden layer	15
Output layer	1
Hidden layer function	Tangent sigmoid
Output layer function	Linear
Number of training epochs	5776
Number of data used for training	123
Number of data used for cross-validation	69
Number of data used for testing	52

Fig. 5 shows the plot of experimental data and % deviation between the experimental and predicted isotherms for the given input conditions during the training process. Fig. 5 also shows the percentage deviation between the experimental and predicted isotherms for the inputs used for cross-validation. It can be observed in Fig. 5 that the percent deviation between n_{exp} and n_{ANN} was found to be less than 5% for most of the input conditions in the training and in the first validation set. Only for three input conditions, specifically at lower pressure, the deviation of n_{exp} and n_{ANN} was found to be $\geq$ 10% during the training and cross-validation process. Considering the performance of neural network globally for a wide range of inputs in both training and testing sets, these outliers could be considered negligible. Neglecting the few outliers, the lower percent deviation between n_{exp} and n_{ANN} suggests that the network is completely trained and is ready for prediction purposes.

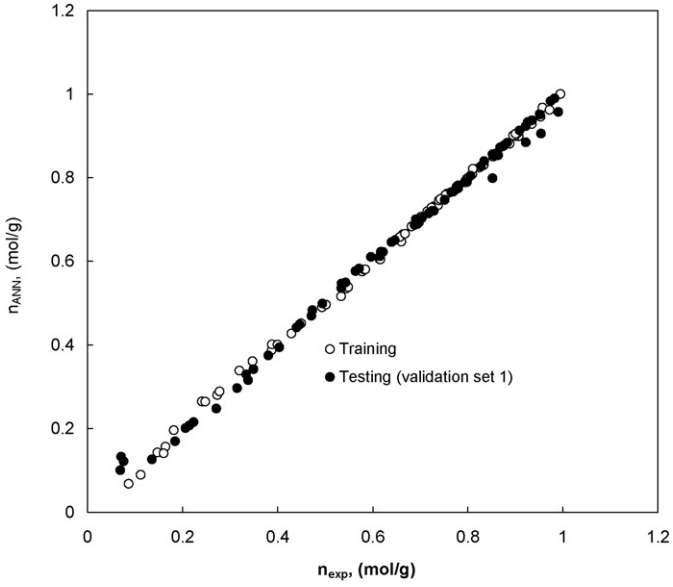

Fig. 4. Plot between experimental and neural network predicted equilibrium sorption isotherm of hydrogen onto pitch-based carbon materials containing metals at equilibrium conditions.

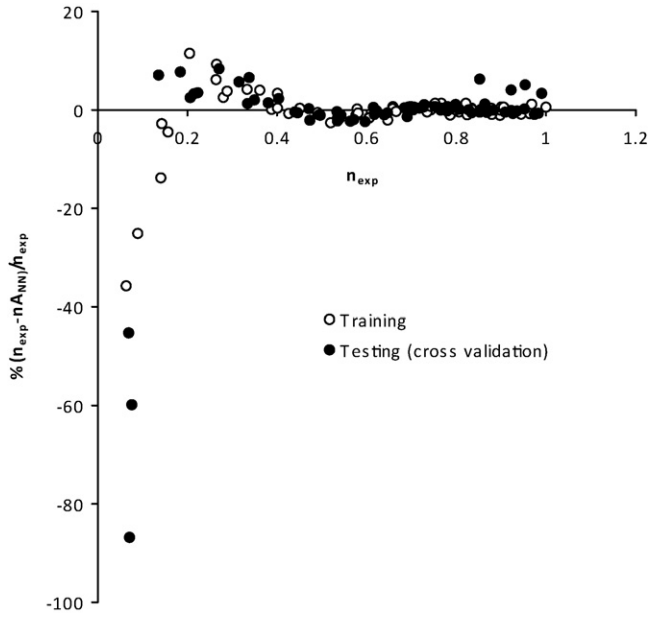

Fig. 5. Percent deviation between the experimental and predicted isotherms versus experimental data during the training and cross-validation process.

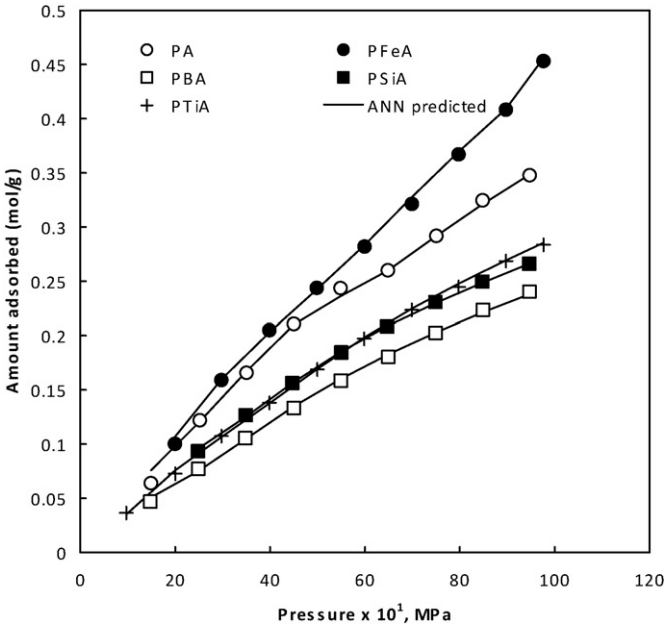

Fig. 6. Experimental and neural network predicted isotherms at 77 K for the given inputs in the second validation set.

4. Validation of the neural network model and testing process

From the design point of view it would be helpful to use *ANN* to predict the amount of hydrogen uptake by carbon materials containing different heteroatoms for any operating conditions. Thus, the constructed network was used to simulate the adsorption system for new input conditions that are kept unaware of the neural network during the training process. The capability of the constructed neural network to predict the equilibrium uptake of hydrogen for the new inputs will also help to identify the robustness and performance of the constructed neural network. For simulation purpose, two validation sets which contain the inputs which were not used in training process were used to predict the hydrogen uptake capacity of the different carbon adsorbents. The first validation set here refers to the data set that is used during the training process for cross-validation.

It is worthwhile to mention that, a separate attempt was initially made by constructing and training the network with equilibrium data at 77 K and it was tested to simulate the hydrogen uptake at 298 K. Unfortunately this network predicted poorly the targets during the testing process. Thus, in this study the network was trained and tested with the equilibrium data obtained at 77 K and 298 K for the studied carbon materials.

Fig. 6 shows the hydrogen experimental and ANN predicted adsorption isotherms for the inputs in the second validation set. Fig. 6 shows that the trained ANN predicted isotherms and the experimental hydrogen sorption isotherms exactly overlap each other. Furthermore, the observations from Fig. 4 suggest that the constructed ANN successfully predicts the hydrogen sorption isotherms for the new inputs in the first validation set which was used for cross-validation. The capability of the trained network in predicting the hydrogen sorption isotherm for the new input condi-

Table 2
Percent deviation between experimental and neural network predicted isotherms by neural network during testing process.

Pressure, MPa	% Deviation	Adsorbent	Pressure, MPa	% Deviation	Adsorbent	Pressure, MPa	% Deviation	Adsorbent
1.49	−18.51	PA	2	−6.74	PFeA	1.48	−7.58	PBA
2.52	0.85	PA	2.97	−0.63	PFeA	2.49	2.80	PBA
3.50	−0.87	PA	3.99	0.91	PFeA	3.48	0.83	PBA
4.50	0.24	PA	4.99	0.51	PFeA	4.50	−1.19	PBA
5.49	3.03	PA	5.99	−0.54	PFeA	5.50	−1.19	PBA
6.48	0.08	PA	6.99	−1.97	PFeA	6.49	−1.44	PBA
7.51	−0.05	PA	7.98	−0.68	PFeA	7.49	−0.19	PBA
8.48	1.08	PA	8.97	−0.19	PFeA	8.49	0.96	PBA
9.47	−0.26	PA	9.77	−0.65	PFeA	9.47	0.92	PBA

Pressure, MPa	% Deviation	Adsorbent	Pressure, MPa	% Deviation	Adsorbent
2.48	−2.42	PSiA	0.97	4.11	PTiA
3.49	1.07	PSiA	2	−4.39	PTiA
4.47	−0.15	PSiA	2.98	0.58	PTiA
5.50	−0.57	PSiA	3.99	0.21	PTiA
6.47	−0.15	PSiA	5	−0.27	PTiA
7.49	0.33	PSiA	5.98	−0.45	PTiA
8.48	0.42	PSiA	6.99	−0.53	PTiA
9.47	−0.10	PSiA	7.97	−1.26	PTiA
			8.97	−0.27	PTiA
			9.76	−0.67	PTiA

tions suggests the robustness of the constructed model. Theoretical or semi-empirical expressions correlating the uptake of hydrogen at equilibrium conditions by carbon materials containing different heteroatoms are not readily available in literature. However, the ANN reported in this work shows that the neural network would be a useful tool to model the hydrogen sorption isotherm onto carbon materials containing different heteroatoms for any condition. In the present study, the neural network was constructed with very few data to model equilibrium hydrogen uptake at two different temperatures. Irrespective of the very low data strength used as inputs during the training process, the ANN performed correctly for the input conditions. Table 2 shows the calculated deviation between the experimental data and the hydrogen uptake predicted by the neural network for the input conditions in the second validation set. It could be deduced from Table 2 and Fig. 5 that the absolute percentage deviation between the experimental and predicted data during the training and testing process was less than 5% for most of the input conditions. Thus, although proposing a purely theoretical model correlating the sorption isotherm for a carbon material containing different heteroatoms would be a very difficult task, the artificial neural network model trained with the physicochemical properties of these carbon materials presented here was successful in solving this difficult task. Though the network was trained with few input data, it is always possible to introduce new inputs to train the network at any time when new experimental data are available. The intent of the future work is to predict the isotherms of other compounds onto these carbon adsorbents. It is also intended to extend the application to model the kinetics of hydrogen onto the same carbon adsorbents doped with different heteroatoms.

5. Conclusions

The application of an artificial neural network to model the adsorption isotherms of hydrogen onto activated carbon containing different heteroatoms was discussed. A feed-forward neural network with a hidden layer using a hyperbolic tangent propagation function and with a linear output layer, was developed and trained to model the adsorption isotherms of hydrogen onto pitch-based carbons containing different heteroatoms. The neural network trained with limited inputs was found to be accurate in representing the experimental data of hydrogen onto carbon materials. The absolute percent deviation between the experimental data and the predicted hydrogen uptake capacity was found to be less than 5% during the training process, irrespective of the input conditions. The constructed ANN successfully simulated the equilibrium hydrogen uptake for the new inputs. The ANN was determined to be robust and sensitive to a wide range of input conditions during the training and testing stages.

The present study is the first step toward the neural network modeling of hydrogen sorption isotherms of activated carbons differing in physicochemical properties.

The ANNs have a number of advantages over the conventional computational systems. The most important advantages are: capacity of synthesizing complex and transparent mappings, rapidity, robustness, fault tolerance, adaptability and small memory requirement.

Though the neural network constructed in this study was based on five different activated carbons, it is always possible to make the constructed neural network more global for other adsorbents by introducing new inputs whenever the new sources are available. The future study is aimed to develop a more global neural network model that could simulate the equilibrium uptake of hydrogen for any sorbents based on the physicochemical properties of these adsorbents and any experimental conditions.

Acknowledgements

Support from the Ministerio de Ciencia e Innovacion (Project MAT2007-61734, Fondos FEDER) and the European Union (Network of Excellence Insidepores, NMP3-CT-2004-500895) are acknowledged. KVK would like to thank Ministerio de Ciencia e Innovacion for the Juan de la Cierva contract. The stimulating suggestions of the reviewers are greatly acknowledged.

References

[1] C. Wu, Q. Gao, J. Hu, Z. Chen, W. Shi, Rapid preparation, characterization and hydrogen storage properties of pure and metal ions doped mesoporous MCM-41, Micropor. Mesopor. Mater. 117 (2009) 165–169.
[2] F.H. Yang, R.T. Yang, Ab initio molecular orbital study of adsorption of atomic hydrogen on graphite: insight into hydrogen storage in carbon nanotubes, Carbon 40 (2002) 437–444.
[3] C.-W. Huang, H.-C. Wu, Y.-Y. Li, Hydrogen storage in platelet graphite nanofibers, Sep. Purif. Technol. 58 (2007) 219–223.
[4] M.M. Castro, M. Martinez-Escandell, M. Miguel-Sabio, F. Rodriguez-Reinoso, Hydrogen adsorption on KOH activated carbons from mesophase pitch containing Si, B, Ti or Fe, Carbon 48 (2010) 636–644.
[5] E. Yoo, T. Habe, J. Nakamura, Possibilities of atomic hydrogen storage by carbon nanotubes or graphite materials, Sci. Technol. Adv. Mater. 6 (2005) 615–619.
[6] L. Wang, R.T. Yang, Hydrogen storage properties of carbons doped with ruthenium, platinum and nickel nanoparticles, J. Phys. Chem. C 112 (2008) 12486–12494.
[7] X. Chen, Y. Zhang, X.P. Gao, G.L. Pan, X.Y. Jiang, J.Q. Qu, F. Wu, J. Yan, D.Y. Song, Electrochemical hydrogen storage of carbon nanotubes and carbon nanofibers, Int. J. Hydrogen Energy 29 (2004) 743–748.
[8] K.Y. Kang, B.I. Lee, J.S. Lee, Hydrogen adsorption on nitrogen-doped carbon xerogels, Carbon 47 (2009) 1171–1180.
[9] A. Gil, R. Trujillano, M.A. Vicente, S.A. Korili, Hydrogen adsorption by microporous materials based on alumina-pillared clays, Int. J. Hydrogen Energy 34 (2009) 8611–8615.
[10] D. Saha, S. Deng, Enhanced hydrogen adsorption in ordered mesoporous carbon through clathrate formation, Int. J. Hydrogen Energy 34 (2009) 8583–8588.
[11] L.L. Vasiliev, L.E. Kanonchik, A.G. Kulakov, D.A. Mishkinis, A.M. Safonova, N.K. Luneva, Newsorbent materials for the hydrogen storage and transportation, Int. J. Hydrogen Energy 32 (2007) 5015–5025.
[12] O.Y. Odunsi, Y. He, T.J. Mays, Hydrogen storage in nanoporous carbons, in: P.L. Llewellyn, F. Rodriguez-Reinoso, J. Rouqerol, N. Seaton (Eds.), Studies in Surface Science and Catalysis, 160, Elsevier, 2007.
[13] Y. Sun, C. Liu, W. Su, Y. Zhou, L. Zhou, Principles of methane adsorption and natural gas storage, Adsorption 15 (2) (2009) 133–137.
[14] X.-Z. Chu, Y.-P. Zhou, Y.-Z. Zhang, W. Su, Y. Sun, L. Zhou, Adsorption of hydrogen isotopes on micro- and mesoporous adsorbents with orderly structure, J. Phys. Chem. B 110 (2006) 22596–22600.
[15] J. Bryjak, K. Ciesielski, I. Zbiciński, Modelling of glucoamylase thermal inactivation in the presence of starch by artificial neural network, J. Biotechnol. 114 (2004) 177–185.
[16] S. Aber, N. Daneshvar, S.M. Soroureddin, A. Chabok, K. Asadpour-Zeynali, Study of acid orange 7 removal from aqueous solutions by powdered activated carbon and modeling of experimental results by artificial neural network, Desalination 211 (2007) 87–95.
[17] K.V. Kumar, K. Porkodi, Modelling the solid–liquid adsorption processes using artificial neural networks trained by pseudo second order kinetics, Chem. Eng. J. 148 (2009) 20–25.
[18] K.V. Kumar, Neural network prediction of interfacial tension at crystal/solution interface, Ind. Eng. Chem. Res. 48 (2009) 4160–4164.
[19] K. Yetilmezsoy, S. Demirel, Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by *Antep pistachio* (*Pistacia vera* L.), J. Hazard. Mater. 153 (2008) 1288–1300.
[20] F. Karaca, B. Ozkaya, NN-LEAP: a neural network-based model for controlling leachate flow-rate in a municipal solid waste landfill site, Environ. Model. Soft. 21 (2006) 1190–1197.
[21] A. Akkoyunlu, K. Yetilmezsoy, F. Erturk, E. Oztemel, A neural network-based approach for the prediction of urban SO_2 concentrations in the Istanbul Metropolitan Area, Int. J. Environ. Pol. 40 (2009) 301–321.
[22] A.H. Mohammadi, D. Richon, Use of artificial neural networks for estimating water content of natural gases, Ind. Eng. Chem. Res. 46 (2007) 1431–1438.
[23] A.D. Naik, S.S. Bhagwat, Optimization of an artificial neural network for modelling protein solubility, J. Chem. Eng. Data 50 (2005) 460–467.
[24] D. Salari, N. Daneshvar, F. Aghazadeh, A.R. Khataee, Application of artificial neural networks for modeling of the treatment of wastewater contaminated with methyl *tert*-butyl ether (MTBE) by UV/H_2O_2 process, J. Hazard. Mater. 125 (2005) 205–210.
[25] M. Martínez-Escandell, P. Torregrosa, H. Marsh, F. Rodríguez-Reinoso, R. Santamaría-Ramírez, C. Gómez-De-Salazar, E. Romero-Palazón, Pyrolysis of petroleum residues: I. Yields and product analyses, Carbon 37 (1999) 1567–1582.

[26] P. Torregrosa-Rodríguez, M. Martínez-Escandell, F. Rodríguez-Reinoso, H. Marsh, C. Gómez de Salazar, E. Romero Palazón, Pyrolysis of petroleum residues: II. Chemistry of pyrolysis, Carbon 38 (2000) 535–546.
[27] F. Rodriguez-Reinoso, J. Garrido, J.M. Martin-Martinez, M. Molina-Sabio, R. Torregrosa, The combined use of different approaches in the characterization of microporous carbons, Carbon 27 (1989) 23–32.
[28] Neural Networks, Statsoft Electronic Statistics Textbook, available online http://www.statsoft.com/textbook/neural-networks.
[29] H. Demuth, M. Beale, Neural Network Toolbox User's Guide. Matlab User's Guide, The Mathworks Inc, Natick, MA, 2000, pp. 5.1–5.75.
[30] I.V. Vetko, D.J. Livingstone, A.I. Luik, Neural network studies. 1. Comparison of overfitting and overtraining, J. Chem. Inf. Comput. Sci. 35 (1995) 826–833.