Trans. Phenom. Nano Micro Scales, 1(1): 19-25, Winter - Spring 2013
DOI: 10.7508/tpnms.2013.01.002

ORIGINAL RESEARCH PAPER

Modeling of Activated Carbon Preparation from Spanish Anthracite Based on ANFIS Structure

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Abstract

Carbon nanostructures are famous structures which are used in several industries such as separation, treatment, energy storage (i.e. methane and hydrogen storage), etc. A successful modeling of activated carbon preparation is very important in saving time and money. There are some attempts to achieve the appropriate theoretical modeling of activated carbon preparation but most of them were almost unsuccessful due to the complexity between the input and output variables. In this paper the empirical modeling of activated carbon preparation from Spanish anthracite based on adaptive neuro-fuzzy inference system (ANFIS) is investigated. ANFIS model is established to delineate the relationship between the BET surface area of the prepared activated carbon with initial and operational conditions; agent type, agent ratio, activation temperature, activation time and nitrogen flow. The results show that the selected model have a good accuracy with a coefficient of determination values (R^2) of 0.9885 and average relative error (ARE) of 0.00268.

Keywords: C*arbon nanostructure; ANFIS; Activated carbon; Neural network*

1. Introduction

Nowadays, carbon nanostructures are using in different processes as an adsorbent or catalyst support [1-3]. Accordingly, this is so natural that finding some economical ways to produce high-quality of these stuffs are the concern of today's scientists and researchers. The stuffs like carbon nanotubes (CNTs), carbon nanofibers and in some ways activated carbons (ACs) could be counted as what so-called carbon nanostructures.

Characterization of carbon nanostructure has always been an interest topic due to decreasing lost of time, money and energy. Even though, numerous methods have been proposed formerly to address the characterization of this kind of materials, no intense theory is still available [4,5]. Although, optimization and characterization of carbon nanostructure have been significantly investigated by many researchers [6-9], the method which used in this research for such application is quite new.

One of the famous carbon structure material is AC. AC is a common adsorbent in various industrial processes such as separation, purification, pollution control and recovery. Due to energy conservation and lower pollution, separation processes are the largest consumer of this kind of adsorbents [10].

The coal and the lignocellulosic materials are commonly used as precursor for the AC fabrication. Lately, numerous efforts to prepare activated carbon from solid waste have been done, but in this study the Spanish anthracite considered as precursor. Among a wide range of coal precursor, anthracites are considered due to their abundance, low cost and high carbon content. Many studies have been handled for the ACs production through chemical activation

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to achieve high capacity storage of hydrogen and methane [7-9, 11, 12].

The purpose of the present work is developing a proper empirical model for AC preparation conditions. This model could help to reach high level of methane uptake through finding the good condition for ACs fabrication. The model was established by the help of artificial intelligence as a strong predicator. Several types of artificial intelligence models have been used for modeling of various chemical engineering processes previously. The adaptive neuro-fuzzy inference system (ANFIS) is utilized in this article to explore the relation between the BET surface area of the prepared carbon structures with some initial and operational conditions such as; agent type, agent ratio, activation temperature, activation time and nitrogen flow.

2. Model specification

Experimental data

The experimental data needed for training and testing the model, are gathered from various published papers [13-16]. In these papers, the Spanish anthracite with a 12.5% of ash content is used as a precursor and the chemical activations with KOH and NaOH are reflected. The specification of the Spanish anthracite is shown in the Table 1.

Several initial and operating conditions could be defined as effective parameters on the BET surface area (S_{BET}) [17], but according to the published data, agent type, agent/coal ratio, activation temperature, activation time and nitrogen flow are selected as input variables in the modeling.

Table 1
Elemental analysis of the Spanish anthracite [13, 15]

Carbon (%)	Hydrogen (%)	Sulphur (%)	Oxygen (%)	Nitrogen (%)
89.66	3.23	0.79	5.10	1.23

ANFIS structure

Fuzzy systems and neural networks are natural complementary tools in building intelligent systems. Neural networks are low-level computational structures which perform well when dealing with raw data. On contrary, fuzzy logic deals with reasoning on a higher level (if-then rules). However, fuzzy systems do not have the ability to learn and cannot adjust themselves accordingly. A neuro-fuzzy system is a neural network that is functionally equivalent to a fuzzy inference model. For example, an adaptive neuro-fuzzy inference system (ANFIS) proposed by Jang [18] is a five-layer feed-forward neural network, which includes fuzzification layer, rule layer, normalization layer, defuzzification layer and a single summation neuron. An ANFIS uses a hybrid learning algorithm that combines the least-squares estimator and the gradient descent method. ANFIS system can incorporate fuzzy IF-THEN rules and also provide fine-tuning of the membership function according to a desired input output data pair.

ANFIS has its advantages and disadvantage. The specific advantages of ANFIS over the two parts of this hybrid system are: "ANFIS uses the neural network's ability to classify data and find patterns. It then develops a fuzzy expert system that is more transparent to the user and also less likely to produce memorization errors than a neural network does. Furthermore, ANFIS keeps the advantages of a fuzzy expert system, while removing (or at least reducing) the need for an expert." However, the problem with the ANFIS design is that a large amount of training data is required to develop an accurate system [19].

The selected ANFIS structure has five inputs (agent type, agent ratio, activation temperature, activation time, and nitrogen flow) and one output (BET surface area). Gaussian function is used as membership function for all inputs and the hybrid learning is employed to have a fast identification of the parameters. The created rules through clustering which are used in the ANFIS model are given in table 2 and the resulted ANFIS structure is shown in Fig. 1.

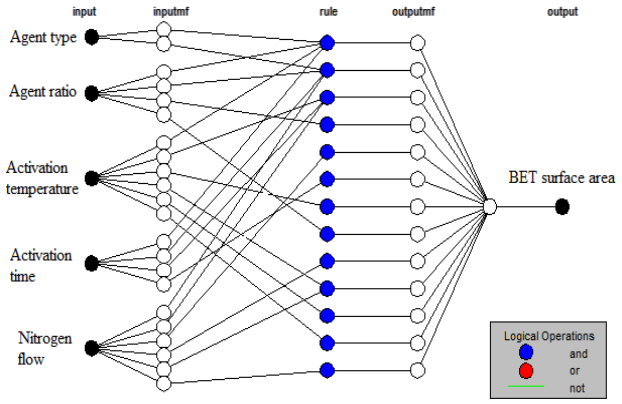

Fig. 1. The structure of the proposed ANFIS model to predict the BET surface area

Table 2
Resulting rules obtained through clustering

Row	Rule*
1.	If (agent type is NaOH) and (agent ratio is M) and (activation temperature is LM) and (activation time is H) then (out1 is out1-cluster1)
2.	If (agent type is KOH) and (agent ratio is L) and (activation time is L) and (nitrogen flow is LM) then (out1 is out1-cluster2)
3.	If (activation temperature is L) and (activation time is M) and (nitrogen flow is VL) then (out1 is out1-cluster3)
4.	If (agent ratio is H) then (out1 is out1-cluster4)
5.	If (nitrogen flow is HM) then (out1 is out1-cluster5)
6.	If (activation time is VL) then (out1 is out1-cluster6)
7.	If (activation temperature is HM) then (out1 is out1-cluster7)
8.	If (agent ratio is VL) then (out1 is out1-cluster8)
9.	If (nitrogen flow is VH) then (out1 is out1-cluster9)
10.	If (activation temperature is H) and (nitrogen flow is H) then (out1 is out1-cluster10)
11.	If (activation temperature is VL) then (out1 is out1-cluster11)
12.	If (activation temperature is VH) then (out1 is out1-cluster12)
13.	If (nitrogen flow is L) then (out1 is out1-cluster13)

* VL= very low, L= low, LM= low medium, M= medium, HM= high medium, H= high, VH= very high

To set up a proper model, the experimental data which are presented in table 3, are disarranged and divided into three categories; 75% allotted for training, 12.5% for validation and 12.5% for testing.

Model performance evaluation

Three error types were devoted to determine the accuracy of the model; average relative error (*ARE*), absolute average relative error (*AARE*) and normalized mean square error (*NMSE*). Additionally, the coefficient of determination values (R^2) was used to demonstrate the precision of simulation. Employing *NMSE* error instead of *MSE* was due to higher values of outputs which were obtained from the model. Naturally, in this case the *MSE* error would be deceptive. These errors are calculated through the following equations:

$$ARE = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{X_{\exp.(i)} - X_{cal.(i)}}{X_{\exp.(i)}}\right) \quad (1)$$

$$AARE = \frac{1}{N}\sum_{i=1}^{N}\left(\left|\frac{X_{\exp.(i)} - X_{cal.(i)}}{X_{\exp.(i)}}\right|\right) \quad (2)$$

$$NMSE = \frac{1}{\sigma^2 N}\sum_{i=1}^{N}\left(X_{\exp.(i)} - X_{cal.(i)}\right)^2 \quad (3)$$

$$R^2 = \frac{\left(\sum XY - n\bar{X}\bar{Y}\right)^2}{\left(\sum X^2 - n\bar{X}^2\right)\left(\sum Y^2 - n\bar{Y}^2\right)} \quad (4)$$

3. Results and discussion

The comparison between the predicted and experimental data for training and testing data sets are shown in Figures 2 and 3, respectively. In addition, the overall performance values; *AARE*, *ARE*, and R^2, are presented in Table 4. It should be noticed that the accuracy of the proposed model is better than the previous modeling studies [20-23].

Table 3
Experimental and predicted data set

Ref.	Agent type	Agent ra	Activation temp. (°C)	Activation time (h)	N_2 flow (ml/min)	S_{BET} (m^2/gr) (Experimental)	S_{BET} (m^2/gr) (Predicted)	Relative Deviation (%)
[13]	KOH	1	730	0.5	500	863	863.0	0.000
[15]	KOH	2	700	0.5	800	1784	2077.3	16.441
[15]	KOH	2	700	1	80	945	945.0	0.000
[15]	KOH	2	700	1	200	1305	1305.1	0.008
[15]	KOH	2	700	1	400	1580	1758.9	11.324
[15]	KOH	2	700	1	800	2021	2020.8	-0.010
[15]	KOH	2	700	2	800	2111	2011.28	-4.726
[13]	KOH	2	730	0.5	400	1637	1637.08	0.002
[13]	KOH	2	730	0.5	500	1938	1938.0	-0.001
[15]	KOH	2	800	1	800	2085	2085.6	0.027
[16]	KOH	3	600	1	400	1330	1712.8	28.781
[16]	KOH	3	680	1	400	2010	2010.0	0.000
[15]	KOH	3	700	1	800	2758	2699.0	-2.139
[13]	KOH	3	730	0.5	500	2746	2746.1	0.004
[14]	KOH	3	730	1	400	2300	2444.5	6.282
[14]	KOH	3	780	1	400	2730	2731.8	0.065
[14]	KOH	3	830	1	400	3290	3290.0	0.000
[15]	KOH	4	700	1	200	2637	2637.0	0.000
[15]	KOH	4	700	1	400	2817	2817.0	-0.001
[15]	KOH	4	700	1	800	3290	3289.5	-0.014
[15]	KOH	5	700	1	800	3183	3293.9	3.484
[13]	NaOH	1	730	0	500	1017	1017.0	0.000
[13]	NaOH	1	730	2	80	118	118.0	-0.007
[13]	NaOH	1	730	2	500	101	101.0	0.003
[13]	NaOH	2	730	0	500	1594	1594.2	0.010
[13]	NaOH	2	730	2	80	334	199.6	-40.226
[13]	NaOH	2	730	2	200	830	830.0	0.000
[13]	NaOH	2	730	2	500	759	759.0	-0.001
[13]	NaOH	3	730	0	500	2208	2208.2	0.009
[13]	NaOH	3	730	0	960	2669	2668.7	-0.011
[13]	NaOH	3	730	2	80	932	932.1	0.010
[13]	NaOH	3	730	2	200	1080	1080.0	0.000
[13]	NaOH	3	730	2	500	1248	1248.1	0.005
[13]	NaOH	4	730	2	80	1045	955.0	-8.611

Table 4
The overall performance values of the ANFIS model

Cluster Radius	Number of MFs	*AARE*	*ARE*	R^2
0.5	13	0.03055	0.002677	0.9885

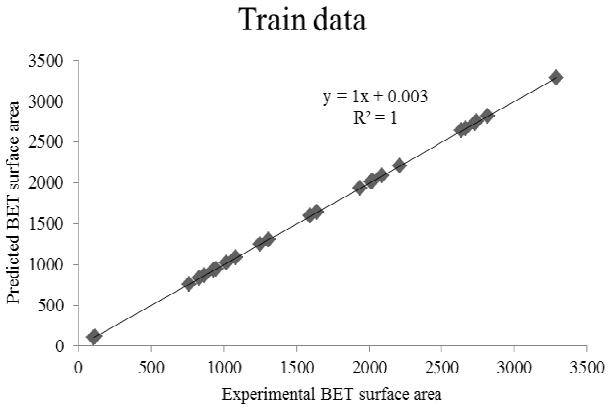

Fig. 2. The comparison between the predicted and experimental data for training data set

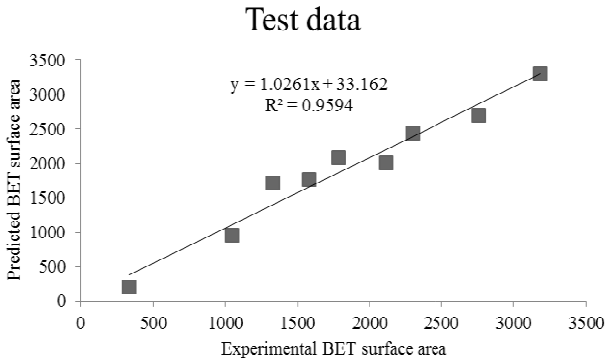

Fig. 3. The comparison between the predicted and experimental data for testing data set

The proposed model can be used for investigating the effects of various inputs on the BET surface area and finding the best operational conditions. For example, Figure 4 indicates the S_{BET} versus agent KOH) ratio and nitrogen flow in constant activation temperature of 700 °C and activation time of one hour. As can be seen, increasing the agent ratio at a constant quantity of nitrogen flow led to the S_{BET} enhancement to a maximum point and it decreased sequentially. Also this figure confirmed that at an activation temperature of 700 ^{o}C and activation time of one hour, the maximum BET surface area can be achieved at an agent ratio of about 4.0 and nitrogen flow greater than 800 ml/min.

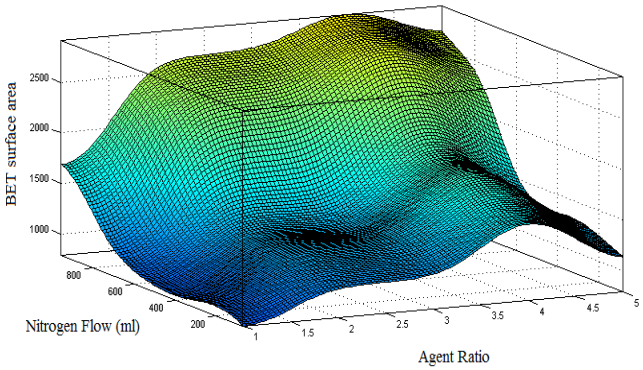

Fig. 4. S_{BET} versus agent ratio and nitrogen flow at activation temperature of 700 °C and activation time of 1 hour (for activation with KOH)

As another example, Figure 5 indicates the S_{BET} versus activation temperature and agent (KOH) ratio. This figure has been depicted for a constant nitrogen flow of 500 ml/min and a fixed activation time of 2 hour. As can be seen, a maximum valve of S_{BET} can be achieved at an agent ratio of about 4.0 and activation temperature greater than 700 ^{o}C.

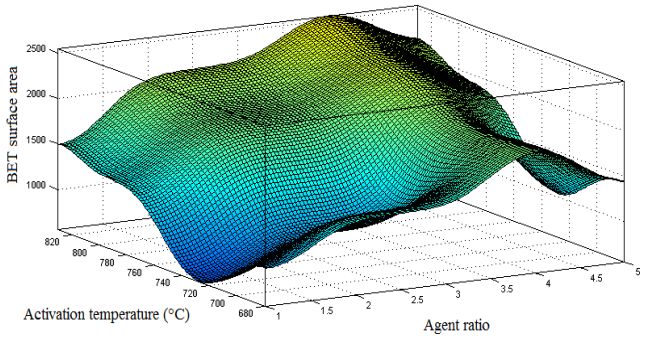

Fig. 5. S_{BET} versus agent ratio and activation temperature at nitrogen flow of 500 ml/g and activation time of 2 hour (for activation with KOH)

4. Conclusion

In this paper the empirical modeling of activated carbon preparation from Spanish anthracite based on adaptive neuro-fuzzy inference system (ANFIS) is investigated. ANFIS model is established to delineate the relationship between the BET surface area of the prepared activated carbon with initial and operational conditions; agent type, agent ratio, activation temperature, activation time and nitrogen flow. The experimental data needed for training and testing the model, are gathered from various published papers [13-16]. The results show that the selected model have a good accuracy with a coefficient of determination values (R^2) of 0.9885 and average relative error (*ARE*) of 0.00268. It should be noticed that the accuracy of the proposed model is better than the previous modeling studies [20-23]. And as a final point, it should be noticed that the high accuracy gained in this research through the ANFIS model, could so hopeful to achieve an economical approach to produce carbon nanostructures.

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