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A novel Approach in Predicting the Adsorption Behavior of Activated and Molecular Sieve Carbons

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Abstract

Artificial neural network (i.e., ANN) method has been adopted in this work to predict the equilibrium adsorption behavior of methane and ethylene for four different carbon adsorbent types. The result has been compared with both empirical models such as Langmuir, Freundlich, UNILAN, Sips and Toth and experimental data. The results revealed that artificial neural network is a powerful and accurate method in predicting the adsorption behaviors of various types of activated and molecular sieve carbons, in contrast with other empirical models and with mean absolute errors of training and testing nets of 0.00000546 and 0.000378.

Keywords: Ethylene, Methane, ANN, Adsorption Isotherm, Molecular Sieve, Activated Carbon.

Introduction

Carbon adsorption has considerable importance to chemical and biochemical engineering and is the most widely used adsorbent. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column [1]. Although, reversible adsorption ability of porous solid has been known from the eighteenth century, the practical applications for separation and purification in industrial scale have recently been developed [2].

In order the separation or purification process to be effective, adsorbent must have high internal volume. These porous materials could be either organic or inorganic in nature, synthetic or natural and in some cases exhibit molecular sieve properties [3]. Adsorbent solids are usually in granular form or porous. The solids must possess certain engineering properties depending upon the application to which they are put. Large surface per unit weight seems essential to all useful adsorbents. Particularly in the case of gas adsorption, the significant surface is not the gross surface of granular particles which are ordinarily used but the very much large surface of the internal pores of the particles. The pores are usually very small, sometimes of the order of a few molecular diameters in width, but their large number provides an enormous surface of adsorption [4].

With the recent interest in the development of new adsorbents and catalysts for gas separation, the problem of accurately estimation the pore size distribution of microporous materials has achieved a certain imperative significance. This is particularly so because of the strong dependence of adsorption and transport characteristics on the structure and pore size of a material. By common convention, microporous materials are those with pore sizes of width less than 2.0 nm. A large number of such materials are in use today for a wide variety of application. These include activated carbon, molecular sieve carbons in the form of pellets as well as cloth fibers and silica-based materials [5].

Theoretically, when the specific surface area of an activated carbon is increased, so does its specific capacitance. But in fact, the specific capacitance change versus the specific surface is much more complex: the nature and the porosity of the precursor pore size distribution, the activation treatment and impurities content are some of the most important parameters that govern the ion adsorption process. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms; and therefore, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding) [4].

Activated carbon is one the most widely used method for adsorption of organic substances. However, no attempts have been made so far to adopt artificial neural network for predictive purposes of such a process. Therefore, it is the aim of the present study to utilize artificial neural network method to predict the equilibrium adsorption behaviors of methane and ethylene on four different carbon adsorbent types and compare it with both empirical models such as Langmuir, Freundlich, UNILAN, Sips and Toth and experimental data.

Empirical Adsorption Isotherm Models

In the analysis of adsorption, it is necessary to have an equation which would correlate equilibrium to the amount of adsorbate and the concentration in the fluid phase, the so called adsorption isotherms. More than 100 isotherm equations in the literature are based on the various physical, mathematical, and experimental considerations. These variances are justified by the fact that different types of adsorption such as solid/gas, solid/liquid, and liquid/gas have apparently, various properties and; therefore, these different phenomena should be discussed and explained with different physical pictures and mathematical treatments [5]. Some of the most such popular mathematical models are discussed here.

1. Langmuir Model

In 1916, Irving Langmuir published a new model isotherm for gases adsorbed on solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent
- Adsorbed molecules do not interact
- All adsorption occurs through the same mechanism

- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent

These four assumptions are seldom all true. There are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb as for the last. The fourth criterion is the most troublesome, as frequently more molecules will adsorb on the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. Often molecules do form multilayers and the Langmuir isotherm is not valid. In 1938 Stephan Brunauer, Paul Emmett, and Edward Teller developed a model isotherm that considers that possibility, so called BET theory. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics (usually called Langmuir-Hinshelwood kinetics) and thermodynamics[1] and is defined as [6]:

$$\frac{C_\mu}{C_{\mu S}} = \frac{b\,p}{1+b\,p} \tag{1}$$

where C_μ is the amount adsorbed, $C_{\mu S}$ is maximum adsorbent capacity for the absorbate, p the pressure and b the parameter model.

2. UNILAN Model

UNILAN equation is a three-parameter equation that often fits data well and is linear in the Henry's law region. It assumes that the adsorbent surface is divided into different sections and ideally over each section, local Langmuir isotherms are applicable and energy distribution is uniformly distributed. In fact, non-homogeneity in the Langmuir equation has been considered in the UNILAN equation as the parameter S and is defined as [6]:

$$\frac{C_\mu}{C_{\mu S}} = \frac{1}{2S}\ln\left(\frac{1+b e^{S}\,p}{1+b e^{-S}\,p}\right) \tag{2}$$

where p is the pressure and S and b are model parameters.

3. Freundlich Model

For a homogeneous flat surface, a classical isotherm (i.e., Freundlich model) is in the form of [6]:

$$C_\mu = k\,p^{1/n} \tag{3}$$

where n is the positive and generally not an integer. The isotherms correspond approximately to an exponential distribution of heats of adsorption. Although lacks the required linear behavior in the Henry's law region, it can often be used to correlate data on heterogeneous adsorbents over wide range of concentration.

4. Sips (or Langmuir- Freundlich) Model

The sips isotherm (or loading ratio correlation with prescribed temperature dependence), is the modified Freundlich model in which the adsorbed amount has a limitation of applying at high pressures (high fluid concentration) and is defined as [6]:

[1] http://en.wikipedia.org

$$\frac{C_\mu}{C_{\mu S}} = \frac{(b\,p)^{1/n}}{1+(b\,p)^{1/n}} \tag{4}$$

where b and n are model constants.

5. Toth Model

Several isotherms combine aspects of both the Langmuir and Freudlich equations. One that has been shown to be effective in describing data mathematically for heterogeneous adsorbents is the Toth isotherms and is defined as [5 and 6]:

$$\frac{C_\mu}{C_{\mu S}} = \frac{b\,p}{\left[1+(b\,p)^t\right]^{1/t}} \tag{5}$$

where b and t are model constants. This three-parameter equation behaves linearly in the Henry's law region and reduces to the Langmuir isotherm for m = 1.

Artificial Neural Network, a Background

Mathematical models and algorithms have been designed to mimic information processing and knowledge acquisition methods of the human brains. These models are called neural networks. Expert systems such as artificial neural network, genetic algorithm and fuzzy logic have been successfully applied in a wide variety of applications in engineering and other research areas. In recent years, neural networks are widely recognized for its ability to interpret pattern based information and ill-posed problems. Furthermore, artificial neural network have been improved extensively in the last past two decades and have been adopted in areas such as pattern recognition, detection of systems, control systems and related fields. Neural network is a new technique which is recommended for simulation of non-linear systems, in non-exact systems or complex systems which does not require an explicit connection between the inputs and outputs. The problems handled by neural networks can be quite varied. In general, they could be divided into four basic types: association, classification (auto or hetro), transformation or mapping (different representation) and modeling. Figure 1 demonstrates a typical connection between layers in a neural network where IW are the weights of input which connects the input to middle layer and LW are the weights of the middle layer and connects the middle layer to output. Furthermore, b1 and b2 signifies the activation function bias for the middle and output layers, respectively and n are the number of neurons of the middle layers which must be optimized for each neural network.

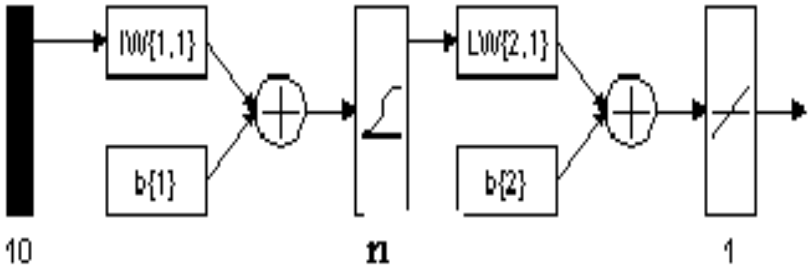


Figure1. A typical flow diagram for the interconnections between layers in a neural network

In adopting neural network, one needs to consider the following steps [7, 8 and 9]:

- How to select the best neural network learning method
- What neural network architecture and which parameters to choose to obtain as much information from the data available as possible
- How to interpret the results obtained to pinpoint the required information best

Modeling and Method of Applications

In this work, adsorption equilibrium isotherms of ethylene and methane gases for four carbon adsorbents types has been estimated using artificial neural network. To assess the precision of the artificial neural networks, the results have been compared with both empirical models such as Langmuir, Freundlich, UNILAN, Sips and Toth and experimental data. The types of adsorbents that have been utilized in this work were activated and molecular sieve carbons. Activated carbons are of the commercial type and made by NORIT and SILICARBON industrial unit and molecular sieve carbons manufactured by TAKEDA industrial unit and IRPI research center (i.e., Iran's Research Institute of Petroleum Industry). In the previous experimental work, it was demonstrated that the adsorption rate is a function of temperature, pressure and the adsorbent capacity [10]. Therefore, in this work these three parameters have been employed for the input to the nets. Each of the adsorbents and adsorbate pair were considered as a system. Consequently, all eights systems were modeled by ANN in the present study. For each system 10 data and a total of 80 data were utilized. To assess the generalization capability of the nets, 70 percent of the data has been chosen for the training and the rest for the testing purposes which were satisfactory. The programs for the systems were written by MATLAB. For modeling purposes, multi layer perceptrron structure (i.e., MLP) and for training the Levenberg-Marquardt algorithm were utilized. For the hidden layer sigmoid function and for the output layer, linear function as a function of activation was employed [9]. Since the nets are highly dependent on the initial weights; therefore, nets with optimum number of neurons in the hidden layer were run several times until the best results were obtained and a final structure of 3:3:1 were achieved.

Results and Discussion

The result of the present study has been compared with both empirical models such as Langmuir, Freundlich, UNILAN, Sips and Toth and experimental data. The accuracy of the nets training and testing is demonstrated in Figures 2 and 3 where the mean absolute errors were 0.00000546 and 0.000378. Table 1 also demonstrates the optimum weight and bias of the middle and output layers for the nets.

To assess the results, a comparative study has also been conducted between the predicted nets values and experimental data for adsorption of ethylene and methane on different adsorbents (Figures 4-7). The results revealed that ANN method is a robust and accurate method in predicting such a process.

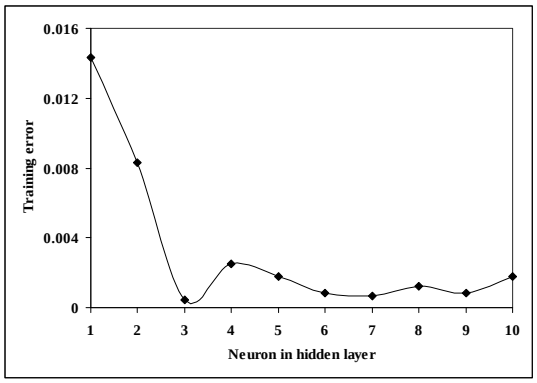


Figure 2. Training errors versus neurons in hidden layer

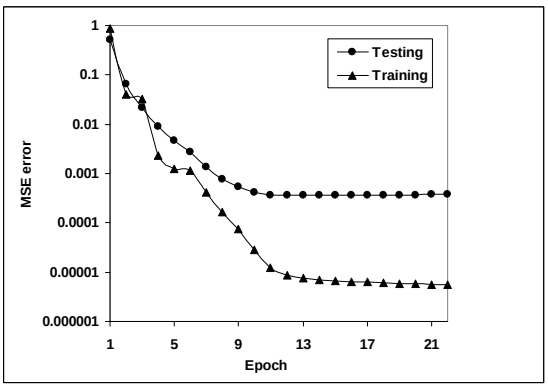


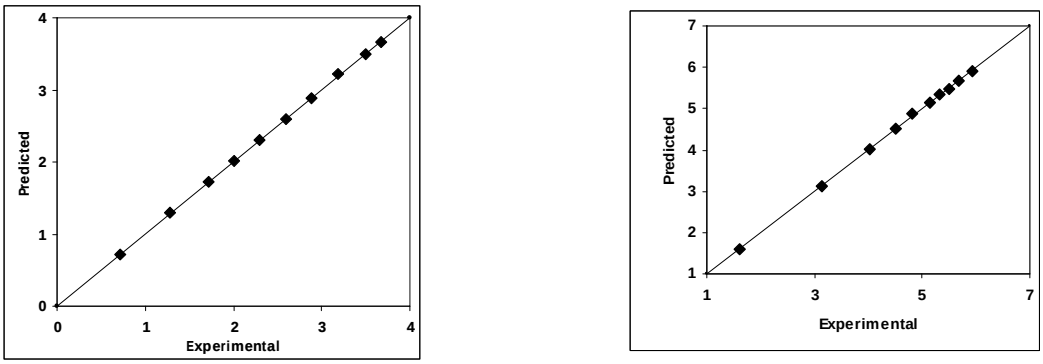
Figure 3. Training and testing errors versus epoch

Table 1. Weight and bias for the middle and output layers

Neurons in the hidden layer	Middle layer weight			Weight of Output layer	Bias of middle layer	Bias of Output layer
1	-2.38403	-2.38403	1.905155	2.246341	-6.01597	-0.2911
2	0.987641	0.987641	-2.94447	-1.44993	-0.98764	-
3	0.177023	0.177023	8.086889	-0.18537	8.222977	-

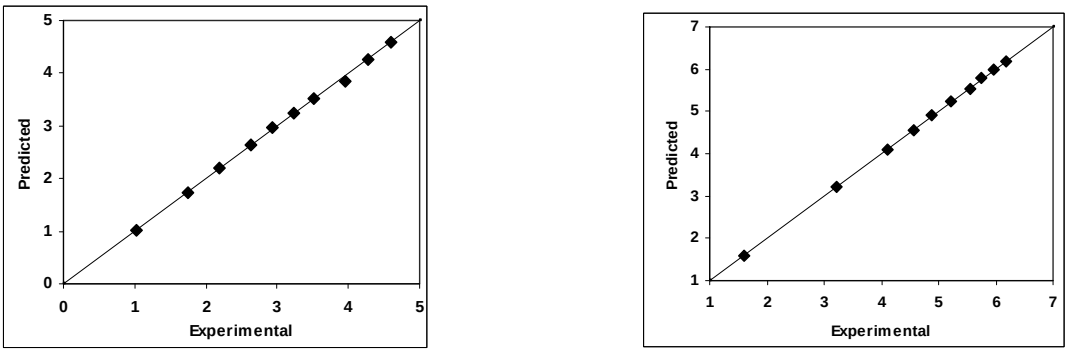
Table 2. Mean absolute errors of the nets and the empirical correlations in the prediction of the equilibrium adsorption behavior of methane and ethylene

Model and type of the gas	ANN	Toth	Sips	UNILAN	Freundlich	Langmuir
Adsorption of ethylene on NORIT	0.25	1.88	1.78	3.16	6.14	1.82
Adsorption of methane on NORIT	0.29	4.17	3.68	7.99	3.36	9.32
Adsorption of ethylene on SILICARBON	0.37	2.62	2.70	3.03	5.80	2.41
Adsorption of methane on SILICARBON	0.55	7.51	5.61	10.16	5.41	11.35
Adsorption of ethylene on TAKEDA	0.44	2.84	3.09	2.12	5.10	4.22
Adsorption of ethylene on TAKEDA	0.32	14.78	2.29	2.56	2.29	2.29
Adsorption of ethylene on IRPI adsorbent	0.20	7.12	5.62	5.97	5.34	11.84
Adsorption of ethylene on IRPI adsorbent	0.19	5.94	5.24	19.25	5.11	10.75



(a) (b)

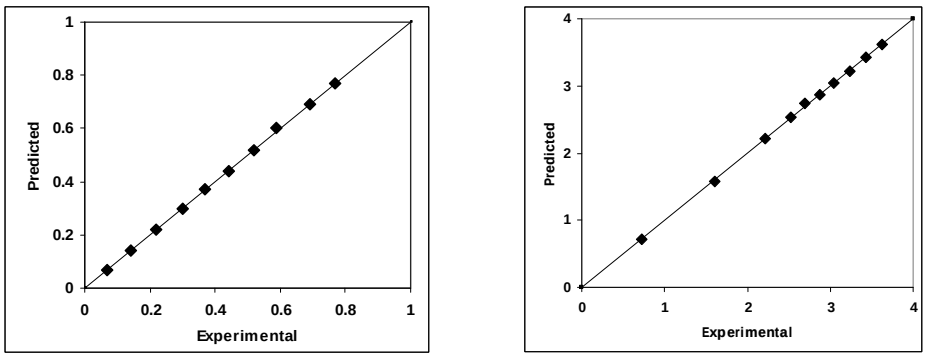
Figure 4. Adsorption of a) methane and b) ethylene on the NORT adsorbent



(a) (b)

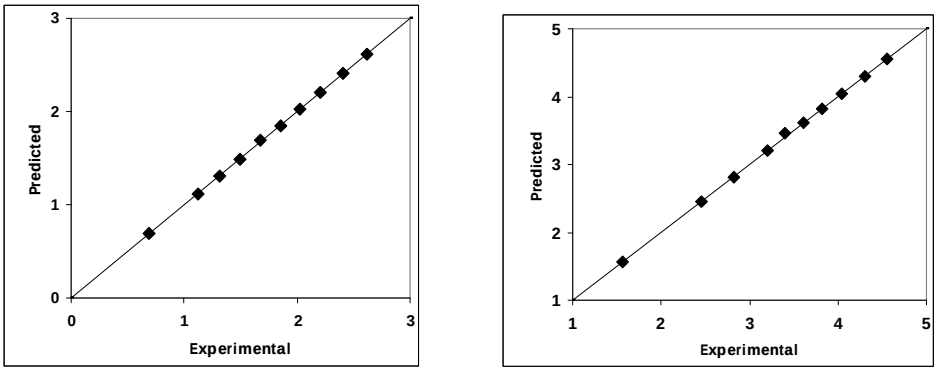
Figure 5: Adsorption of a) methane and b) ethylene on the SILICARBON adsorbent

To evaluate the accuracy of the predicted nets values, a comparative study between the mean absolute errors obtained from the nets and the empirical correlations which are demonstrated in Table 2. It could also be noted from Table 2 that the ANN method could predict the equilibrium adsorption behavior of methane and ethylene with a good degree of accuracy, in contrast with the other empirical correlations.



(a) (b)

Figure 6: Adsorption of a) methane and b) ethylene on the TAKEDA adsorbent



(a) (b)

Figure 7: Adsorption of a) methane and b) ethylene on the IRPI adsorbent

Conclusions

The aim of this work was to utilize artificial neural network method in predicting the equilibrium adsorption behavior of methane and ethylene on four different carbon adsorbent types. The result of the present study has been compared with both empirical models such as Langmuir, Freundlich, UNILAN, Sips and Toth and experimental data. The finding of this research revealed that the accuracy of nets training and testing was high and with mean absolute errors of 0.00000546 and 0.000378. This work also shows that ANN method predicts the equilibrium adsorption behaviors of IRPI's adsorbents for both ethylene and methane with a good degree precision. Furthermore, it revealed that Langmuir model was not a suitable model for predicting purposes, since the experiments have been carried out at high pressure and that the model deviates from a single layer adsorption behavior. Moreover, Freundlich and Sips models have also some limitations and UNILAN model assumes ideal conditions. On contrast, the ANN method has no limitation; and could be utilized to predict the behavior of a single and multi adsorption layer for different adsorbents and adsorbates.

Therefore, the findings of the present study reveals that artificial neural network method could provide an accurate and robust technique in predicting the equilibrium adsorption behavior for methane and ethylene gases for different carbon adsorbent types.

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