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Global statistical predictor model for characteristic adsorption energy of organic vapors–solid interaction: Use in dynamic process simulation

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ABSTRACT

Adsorption of Volatile Organic Compounds (VOCs) is one of the best remediation techniques for controlling industrial air pollution. In this paper, a quantitative predictor model for the characteristic adsorption energy (E) of the Dubinin–Radushkevich (DR) isotherm model has been established with R^2 value of 0.94. A predictor model for characteristic adsorption energy (E) has been established by using Multiple Linear Regression (MLR) analysis in a statistical package MINITAB. The experimental value of characteristic adsorption energy was computed by modeling the isotherm equilibrium data (which contain 120 isotherms involving five VOCs and eight activated carbons at 293, 313, 333, and 353 K) with the Gauss–Newton method in a statistical package R-STAT. The MLR model has been validated with the experimental equilibrium isotherm data points, and it will be implemented in the dynamic adsorption simulation model PROSIM. By implementing this model, it predicts an enormous range of 1200 isotherm equilibrium coefficients of DR model at different temperatures such as 293, 313, 333, and 353 K (each isotherm has 10 equilibrium points by changing the concentration) just by a simple MLR characteristic energy model without any experiments.

1. Introduction

The Volatile Organic Compounds (VOCs) removal is of main interest for air cleaning up and purification. As a VOCs removal technique, adsorption processes as Vacuum Temperature Swing Adsorption (VTSA) or Temperature Swing Adsorption (TSA) appear to be very useful to perform these pollutants abatement [1,2]. But the design of such processes requires adsorption experimental thermodynamic data, which can be obtained with difficulties. Thus, the use of predictive models could be valuable to reduce the experimental measurements. Adsorption isotherm models have been developed to represent the adsorption equilibrium data in mathematical forms with different theories behind it. The isotherm models are generally derived from the fundamental equation of Gibbs isotherm [3]. Several isotherm models have been established such as Langmuir, BET, Freundlich, Langmuir–Freundlich, and Dubinin–Radushkevich (DR) to model the adsorption phenomena [3,4].

During dynamic adsorption, the temperature rise at different sections of the adsorbent bed depending on the properties of Volatile Organic Compounds (VOCs), on the characteristics of the adsorbent, and also on the interactions between the VOCs and the adsorbent. The increase in temperature in the adsorbent bed is caused due to the integral amount of adsorption heat [5–13]. While constructing a mathematical equilibrium expression for adsorption isotherm, the following factors were considered as important [14]:

1. The enthalpy of adsorption.
2. The pore size distribution function of the adsorbent.
3. The ability of adsorbate to condense within the pore of certain size.
4. The adsorbate affinity itself, which would have an impact on the thickness of the adsorption layer.

The theories behind the isotherm models have already been extensively discussed in the literature [15–24]. In this research work, five VOCs and eight activated carbons have been studied. The adsorption isotherm experiments for each VOC–activated carbon system have been performed at four different temperatures (293, 313, 333, and 353 K). We chose to focus on the DR isotherm model, because (1) the DR isotherm model is based on the potential theory developed by Polányi and the pore volume filling theory

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Nomenclature

C_o	initial concentration of VOC injected (mol m^{-3})	V	volume of the reactor (m^3)
C_e	equilibrium concentration of VOC (mol m^{-3})	W_o	volume of micropore (cm^3 g^{-1})
E	characteristic adsorption energy of DR model (kJ mol^{-1})	α	VOC polarizability (10^{-24} cm^3)
m	mass of activated carbon (kg)		
Pa	parachor of the VOC (cm^{-3} g$^{0.25}$ s$^{-0.5}$ mol^{-1})		
P_s	saturation pressure (kPa)		

by Dubinin [15–24] see Eq. (1); (2) the DR isotherm model has only two coefficients (W_o) and (E), and so the model remains simple.

$$q_e = \frac{W_o}{V_m} \cdot \exp\left(-\left(\frac{\mathrm{RT}}{E}\ln\left(\frac{p_s}{p_e}\right)\right)^2\right) \quad (1)$$

W_o is the microporous volume that can be filled by adsorbate (cm^3 g^{-1}), V_m is the molar volume of the adsorbed phase (cm^3 mol^{-1}), E is the characteristic energy, *that is,* the adsorption potential of the couple adsorbent–adsorbate (kJ mol^{-1}), and p_s is the vapor saturation pressure of the adsorbate (Pa).

The objectives in this research paper are as follows: (1) modeling of isotherm equilibrium data with the isotherm models by using Gauss-Newton method in statistical analysis language R-STAT; (2) establishing Multiple Linear Regression (MLR) model for the characteristic adsorption energy (E) of Dubinin–Raduskevich (DR) isotherm by using MLR analysis tool in MINITAB statistical software; (3) the MLR model is validated by comparing them with the experimental values of the coefficients that are obtained by modeling with R-STAT; and (4) this MLR model will be then implemented in the dynamic adsorption simulation model PROSIM (commercial software). This MLR model implementation step would enable the dynamic simulation PROSIM to avoid the use of experimental results of isotherm equilibrium data, and it makes the simulation tool simpler and efficient.

2. Experimental

2.1. Selection of VOCs and activated carbons

The choice of five VOCs and eight activated carbons had been made to cover the wide range of such as (1) nature of family of VOCs; (2) properties of VOCs; (3) the VOCs that are used as solvents and reactants in chemical/food/hydrocarbon industries; (4) characteristics of the activated carbons; (5) mode of activation of activated carbons; (6) raw material of activated carbons; and (7) manufacturer of the activated carbons. Table 1 shows the selected VOCs and their physical properties that were essential to establish the MLR models.

2.2. Characteristics of activated carbon

The physical properties of the activated carbons such as BET surface area and micropore volume were determined by Horvath–Kawazoe method and were measured by nitrogen adsorption isotherm at 77 K (Micromeritics ASAP 2010) [3,4,25]; the meso- and macropore volumes and bulk density were measured by using mercury porosimeter (Micromeritics Autopore IV 9500) [26]. Table 2 summarizes the results of characteristics of the activated carbons.

Table 1
Properties of VOCs.

Compounds	Family nature	Molecular weight	Parachor
		(g mol^{-1})	cm^{-3} g$^{0.25}$ s$^{-0.5}$ mol^{-1}
Dichloromethane	Chloro	84.93	147.9
Toluene	Aromatic	92.14	244.6
Ethanol	Alcohol	46.07	128.3
Ethyl formate	Ester	74.08	177.6
Acetone	Ketone	58.08	162.8

2.3. Adsorption isotherm measurements

The volumetric apparatus used to perform adsorption isotherm measurements has been shown in Fig. 1. 0.2 g of each activated carbon was placed in 10 glass reactors of 2.1 L size. A known volume of VOC had been injected in glass reactors in the range of 20-400 μL. After equilibrium is reached (after 8 hours based on preliminary experiments), a part of the gas phase was sampled (3 times for measuring error deviation) and analyzed using a gas chromatograph to establish the VOC gas phase concentration (Ce). The adsorbed amount of VOC was determined by mass balance according to Eq. (2) [4], where C_0 is the injected VOC concentration, V is the volume of the reactor containing the AC, and m is the adsorbent mass.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

The R-STAT [1] statistical software package was then used to check the significance of the computed parameters using an interval of confidence of 95% by student t-test.

2.4. Multiple Linear Regression procedure [27]

Multi Linear Regression (MLR) is a standard procedure that enables to understand the most significant variables (from the characteristics of activated carbon and properties of activated carbon) on the measured response. The discrimination of less significant variables makes the MLR model more statistically reliable, and so, it could be applied to a wide range of VOC–activated carbon systems. The MLR models had been established by using the statistical package MINITAB. The MLR model of the characteristic adsorption energy [E] of DR model is established as a function of the properties of VOCs and the characteristics of the activated carbons. The F-test had been used on each of the parameters in the MLR model to test the statistical significance of the model under 95% confidence of interval.

3. Results and discussion

3.1. Results of adsorption isotherm curves at different temperatures

Fig. 2 shows an example of adsorption isotherm results at 293, 313, 333, and 353 K for the adsorption system of dichloromethane—Pica BC 120. The AC adsorption capacities decrease when the temperature increases as shown in Fig. 3. The error bars in Fig. 2 have been calculated by using the classical error propagation method. The errors were based on the accuracy of: (1) volume of injection of VOC with the syringe; (2) mass of