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A Statistical Approach to Determine Optimal Models for IUPAC-Classified Adsorption Isotherms

Md. Matiar Rahman ^{1,2,3}, Mahbubul Muttakin ², Animesh Pal ^{2,4}, Abu Zar Shafiullah ⁵ and Bidyut Baran Saha ^{1,2,*}

- ¹ Mechanical Engineering Department, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan; matiar@du.ac.bd
- ² International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan; mahbubul.muttakin@gmail.com (M.M.); animesh@kyudai.jp (A.P.)
- ³ Department of Statistics, University of Dhaka, Dhaka-1000, Bangladesh
- ⁴ Department of Nuclear Engineering, University of Dhaka, Dhaka-1000, Bangladesh
- ⁵ Department of Statistics, University of Auckland, Auckland-1010, New Zealand; asha902@aucklanduni.ac.nz
- * Correspondence: saha.baran.bidyut.213@m.kyushu-u.ac.jp; Tel.: +81-92-802-6722

Received: 15 October 2019; Accepted: 27 November 2019; Published: 29 November 2019

Abstract: Adsorption heat transformation (AHT) systems can play a major role in protecting our environment by decreasing the usage of fossil fuels and utilizing natural and alternative working fluids. The adsorption isotherm is the most important feature in characterizing an AHT system. There are eight types of International Union of Pure and Applied Chemistry (IUPAC) classified adsorption isotherms for different "adsorbent-adsorbate" pairs with numerous empirical or semi-empirical mathematical models to fit them. Researchers face difficulties in choosing the best isotherm model to describe their experimental findings as there are several models for a single type of adsorption isotherm. This study presents the optimal models for all eight types of isotherms employing several useful statistical approaches such as average error; confidence interval (CI), information criterion (ICs), and proportion tests using bootstrap sampling. Isotherm data of 13 working pairs (which include all eight types of IUPAC isotherms) for AHT applications are extracted from literature and fitted with appropriate models using two error functions. It was found that modified Brunauer–Emmet–Teller (BET) for Type-I(a) and Type-II; Toth for Type-I(b); GAB for Type-III; Ng et al. model for Type-IV(a) and Type-IV(b); Sun and Chakraborty model for Type-V; and Yahia et al. model for Type-VI are the most appropriate as they ensure less information loss compared to other models. Moreover; the findings are affirmed using selection probability; overall; and pairwise proportion tests. The present findings are important in the rigorous analysis of isotherm data.

Keywords: bootstrap sample; information criterion; isotherm model; IUPAC; optimum isotherm

1. Introduction

To reduce global electricity demand, scientists are paying considerable attention to adsorption heat transformation (AHT) technologies such as cooling and heating as they can be driven by renewable energy or waste heat having a temperature of as low as 60 °C [1]. Waste heat [2–6] or heat from cost-effective non-concentrating solar thermal collectors [7–10] can be utilized for this purpose. The principal component of anAHT system is its adsorption chamber, which is a heat exchanger in which the adsorbent materials are placed. The chamber goes through adsorption and desorption

processes in cycles to provide thermal compression of the working fluid or adsorbate vapor. The significant factor affecting the performance of AHT is the "adsorbent-adsorbate" pair [11,12]. The fundamental characteristics of the "adsorbent-adsorbate" pair can be found by analyzing adsorption isotherm and kinetic models. The parameter values of the optimal isotherm model are needed for further analysis, like system design or simulation.

An adsorption isotherm provides information about the maximum amount of adsorbate that can be absorbed by the adsorbent at a particular pressure. In order to standardize experimental data of different "adsorbent-adsorbate" pairs, it is essential to correlate them with different isotherm models. Based on the nature of adsorption isotherms, the International Union of Pure and Applied Chemistry (IUPAC) [13,14] classifies adsorption pairs into eight different types, as can be seen in Figure 1. Type-I(a) isotherm is found for narrow microporous adsorbent having a pore size < ~1 nm. The Type-I(b) isotherm is mainly characterized by monolayer adsorption. The uptake continuously increases with pressure and reaches a plateau at saturation pressure. Type-II isotherm is characterized by multilayer adsorption [15] and nearly analogous to the Type-I(b) shape; the only difference between the two is the absence of the plateau in Type-II. The uptake continuously increases even when the pressure ratio is close to unity. The shape of the Type-III adsorption isotherm is convex [15,16]. At low pressures, the uptake is low, but it increases sharply at high pressures. Depending on the pore width, Type-IV isotherm is divided into two types, one with hysteresis and another without hysteresis, i.e., Type-IV(a) (pore width greater than 4 nm) and Type-IV(b) (pore width smaller than 4 nm), respectively. Type-IV(b) is observed for the adsorbent having cylindrical and conical mesoporous with a smaller width, which is entirely reversible closed at the tapered end. Type-V is distinguished by its characteristic S-shaped isotherm, and it also demonstrates a hysteresis loop. Finally, in Type-VI, the adsorption occurs in steps.



Figure 1. Physisorption isotherms classification (©2015 IUPAC) [14]. B symbolizes monolayer formation.

Generally, isotherm data are correlated by applying various isotherm models where the bestfitted model is used to analyze the adsorption behavior. From the literature studies, it is found that different pairs exhibit different types of adsorption isotherms, and numerous authors had tried to get the best-fitted model for those [17]. Table 1 summarizes the different adsorption pairs with their isotherm type and the fitted model.

Adsorption Pair	Type	Best Fitted Model	Reference
(i) Carbon K4-700/N2 at 77 K			(i) Hu et al. [18]
(ii) BIDC-1-700/Ar at 87 K (pore size less than 1 nm	Type-I(a)	Fitted model is not available	(ii) Cychosz et al.
for both (i) and (ii)).			[19]
 (i) Maxsorb III/ethanol (ii) Silica gel/water (iii) Carbon based composite/CO2 (iv) WPT-AC/ethanol (v) M-AC/ethanol (vi) Zeolite/water at 25 °C (vii) (SRD 1352/3, FR 20, ATO and AP4-60/COCL-1200)/ N2 * (viii) Carbon based composite/CO2 (ix) Ionic liquid binder based composite/ethanol (x) Silica gel based composite/water 	Type-I(b)	 (i) D–A model (ii) Tóth (iii) Tóth (iv) D–A and Tóth (v) D–A and Tóth (vi) Tóth (vii) D–A (vii) D–A and Tóth (ix) D–A (x) Tóth 	 (i) El-Sharkawy et al. [20] (ii) Rahman et al. [21] (iii) Pal et al. [22] (iv) Pal et al. [23,24] (v) Pal et al. [23,24] (vi) Wang et al. [25] (vii) Brancato et al. [26] (viii) Berdenova et al. [27] (ix) Pal et al. [28] (x) Younes et al. [29]
(i) PBA/water at 25 °C (ii) Alumina/water at 20 °C (iii) PCB/water at 22 °C	Type-II	(i) GAB model (ii) BET model (iii) Not fitted	(i) Sultan et al. [30] (ii) Naono et al. [31] (iii) Wang et al. [32]
(i) ACP/water at 30 °C (ii) Dried fruits/moisture	Type-III	(i) D–A model (ii) GAB model	(i) Sultan et al. [30] (ii) Maroulis et al. [33]
(i) Oxidized carbon/water (ii) PVDC/water at 35 °C iii) Tripolis/water at 21 °C	Type-IV(a)	(i) Do et al. model (ii) Do et al. model (iii) BET model	(i) Do et al. [34] (ii) Do et al. [34] (iii) Rakitskaya et al. [35]
(i) IRMOF-74-V-hex/argon at 87 K(ii) IRMOF-74-V-hex/nitrogen at 77 K (pore size less than 4 nm)	Type-IV(b)	The fitted model is not available	(i) Cho et al. [36] (ii) Cho et al. [36]
 (i) ACF/water at 30 °C (ii) Hydrophobic carbon/water (iii) AQSOA-Z01/water and AQSOA-Z02/water (iv) Ferroaluminophosphate/water (v) AQSOA zeolite/ water (vi) AIPO-18, FAPO-34, SAPO-34/water (i) MgO (100)/methane 	Type-V	 (i) D-A model (ii) Do et al. model (iii) D-A, modified Langmuir (iv) Hybrid model (v) D-A, modified Langmuir, Sun and Chakraborty (vi) D-A model (i) Ne et al model 	(i) Sultan et al. [30] (ii) Do et al. [34] (iii) Kayal et al. [37] (iv) Kim et al. [38] (v) Teo et al. [39] (vi) Brancato et al. [40] (i) Ng et al. [41]
(ii) Exfoliated graphite/methane	Type-VI	(ii) Yahia et al. model	(ii) Yahia et al. [42]

Table 1. Examples of adsorption pair to correspond isotherm type and the fitted mode
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* Activated carbon from various biomass sources.

Thus, from the above literature reviews, it is evident that many adsorption isotherm models had been suggested for different types of IUPAC classified isotherms, but there is no widely accepted model for any specific isotherm type. Moreover, there is no model fitted yet for Type-I(a) and Type-IV(b) isotherm. Furthermore, there is also a lack of explanation about the determination of the most suitable model for any type of adsorption isotherm considering the statistical analysis of the best-fitted model. In almost all the cases, to the best of our knowledge, authors did not consider the information loss of the fitted model, and they used only root mean square deviation (RMSD) error analysis in their investigations. RMSD does not even consider the number of parameters of the

fitted model. Besides, different scientists proposed several models for a particular type of isotherm. For example, authors [43] proposed D–A, Tóth, Langmuir, Modified D–A for Type-I(b). Firstly, several models are fitted by the researcher for specific experimental data, and then based on RMSD, the researcher makes a decision for the optimal model, which is tedious work. The main aim of the current study is to find out optimal models for all the eight types of isotherms employing several statistical tools such as average error, confidence interval (CI), information criterion (IC's), and proportion tests using bootstrap sampling. In the current study, two error functions, RMSD and hybrid fractional error deviation (HYBRID) used to optimize the parameters for Type-I(a) and Type-I(b) adsorption isotherm. Whereas, on the other hand only HYBRID error evaluation function is used for other types since authors [21] showed that HYBRID error was better than other errors for optimization of parameters. Parameter effect adjustment and information loss are considered in this investigation to find the optimal isotherm model for a particular type, which also makes it significant from the statistical analysis of the best-fitting model.

In this study, 13 relevant isotherm data of "adsorbent-adsorbate" pairs are extracted from the literature for identifying optimal models for IUPAC classified eight types of isotherms. Statistical information criteria using a bootstrap sample have been used to select the optimal isotherm model for all IUPAC classified adsorption isotherms. Section 2 of this article describes different isotherm models and the corresponding equations used in this study. Error evaluation functions and descriptions of statistical tools are narrated in Sections 3 and 4, respectively. In R-programming, 1000 (large sample size) bootstrap samples (n = 1000) are taken, and the distribution of n = 1000 bootstrap errors is constructed to validate the use of model selection criteria, which are used for finding the optimal isotherm model. The probability of optimal model selections is also calculated. Finally, overall and pairwise proportion tests are conducted, for the equality of minimum information criterion, to identify the statistically significant optimal models for all types of IUPAC classified isotherms.

2. Adsorption Isotherm Models

The maximum amount of adsorbate that can be adsorbed by the adsorbent at specific pressure and temperature is known as the equilibrium uptake. This equilibrium uptake at a particular temperature can be represented by an isotherm model that shows the change in uptake with pressure. Various isotherm models are given by scientists to simulate the adsorption characteristics of different adsorption pairs.

2.1. Dubinin-Astakhov (D-A) Model

The Dubinin–Astakhov (D–A) model [44] is widely used in the adsorption of water and several gases on carbon-based adsorbent [25]. Carbonaceous solids resulting from a high degree of burn-off during activation; for these consequences, heterogeneity increases; in this case, the D–A model is used [45]. The model can be expressed by,

$$\frac{W}{W_0} = \exp\left[-\left\{\frac{RT}{E}\ln\left(\frac{P_s}{P}\right)\right\}^n\right]$$
(1)

where, *W* is the instantaneous uptake in [g/g], W_0 denotes maximum uptake [g/g], *E* is the characteristic energy [kJ/mol] and *n* is the heterogeneity parameter [–]. P is the pressure [kPa], and P_s denotes saturated vapor pressure [kPa]. When n = 2, the D–A model reduces to the Dubinin–Radushkevic (D–R) model.

2.2. Modified Dubinin-Astakhov (D-A) Model

In the D–A model, P_s denotes the saturated vapor pressure at temperature T. The critical point, T_c of CO₂ is 31 °C. So above this point, the liquid state does not exist. In such a case, the saturated vapor pressure is replaced by the pseudo saturated vapor pressure determined by [46,47],

$$P_s = \left(\frac{T}{T_c}\right)^k P_c \tag{2}$$

where k is the parameter indicating the interaction between adsorbate and adsorbent. The modified D–A model can be written as,

$$q = \frac{W_0}{V_m} \exp\left[-\left\{\frac{RT}{E}\ln\left(\frac{P_s}{P}\right)\right\}^n\right]$$
(3)

where *q* is the instantaneous adsorbed phase volume (cm³/g), W_0 denotes maximum micropore volume (cm³/g). The molar volume V_m of the adsorbed phase is estimated using properties of CO₂ at triple point and coefficient of thermal expansion which is given by Ozawa et al. [48],

$$V_m = V_t \exp\left[\alpha \left(T - T_t\right)\right] \tag{4}$$

where T_t and V_t denote temperatures and molar volume of the liquid adsorbate at the triple point, respectively, α is the thermal expansion coefficient of the superheated liquid and $\alpha = \frac{1}{T}$. For CO₂ adsorption onto activated carbon, the values observed are $V_t = 0.84858$ cm³/g, $T_t = 216.6$ K and $\alpha = 0.0025 \frac{1}{K}$ [49].

2.3. Tóth Model

The Tóth model [43] performs well in estimating the adsorption uptake both in low pressure and in high-pressure regions. It describes well many systems with sub-monolayer coverage. It can be expressed by,

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q}{RT}} P}{\left[1 + \left(b_0 e^{\frac{Q}{RT}} P\right)^t\right]^{\frac{1}{T}}}$$
(5)

where b_0 is the equilibrium constant [1/kPa], Q is the isosteric heat of adsorption [J/mol], and R is universal gas constant [J/(mol.K)]. The parameter t is supposed to characterize the system heterogeneity. If it deviates further from unity, the system is said to be more heterogeneous [45].

2.4. Langmuir Model

The Langmuir model [50] assumes that all sites of adsorbents are energetically equivalent and identical, i.e., homogeneous, and each site is occupied only by one atom [45]. It can explain well the monolayer adsorption process. When t = 1, the Tóth model reduces to the Langmuir model and can be expressed as,

$$\frac{W}{W_0} = \frac{b_0 e^{\frac{Q}{RT}} P}{1 + b_0 e^{\frac{Q}{RT}} P}$$
(6)

The Modified Langmuir model [37,51] was developed based on the Fermi-Dirac distribution function that includes the interaction between refrigerant and adsorbent, loading, and surface heterogeneity factors. It can be described by,

$$\frac{W}{W_0} = \frac{\beta\left(\frac{P}{\varphi^*}\right)}{\left[1 + \left(\beta^m - \alpha\right)\left(\frac{P}{\varphi^*}\right)^m\right]^{\frac{1}{m}}}$$
(7)

where, $\frac{P}{\varphi^*} = \left(\frac{P}{P_s}\right) \exp\left\{\frac{\phi_m}{RT} \left\{1 - \left(\frac{P}{P_s}\right)^n\right\} + z\right\}.$

where, β is load factor [–], z is compressibility factor [–], α is a coefficient[–], ϕ_m is minimum potential energy [J/mol], m is heterogeneity factor or mass [kg] and n is adsorbate-adsorbent interaction factor[–].

2.6. Freundlich Model

The Freundlich model [24,52] is the most primitive model that describes the adsorption mechanism and assumes that the surface is heterogeneous for energy distribution; also, surface topography is patchwise [45]. It can be written as,

$$\frac{W}{W_0} = \left(\frac{P}{P_s}\right)^{\frac{1}{n}}$$
(8)

Generally, the parameter n is greater than unity [45]. Freundlich model turns into Henry's law if n = 1, which works very well to simulate the adsorption uptake in the low- pressure region.

2.7. Hill Model

The binding capability of the different gas molecules onto homogeneous adsorbent can be described by the Hill model. The model adopts that adsorption is a cooperative phenomenon, with the ligand-binding capacity at one site on the macromolecule, which may impetus different binding sites on the same macromolecule [53]. It is a three-parameter model that combines properties of Langmuir and Freundlich isotherms and can be expressed as,

$$\frac{W}{W_0} = \frac{\left(\frac{P}{P_s}\right)^{n_H}}{K_D + \left(\frac{P}{P_s}\right)^{n_H}}$$
(9)

where, n_H and K_D represent the Hill cooperativity coefficient of the binding interaction [–] and Hill constant [–] respectively. Here $n_H > 1$ indicates positive binding, $n_H = 1$ is used for non-cooperative binding and $n_H < 1$ indicates negative cooperativity in binding.

2.8. Mahle Model

The Type-V adsorption isotherm is characterized by its typical S-shape. It assumes to describe a pore scattering that would be occupied by capillary condensation. Mahle [54] developed a model that explains a Type-V adsorption isotherm. It can be expressed as,

$$\frac{W}{W_s} = \frac{1}{C} \left[\tan^{-1} \left(\frac{x - A}{B} \right) - \tan^{-1} \left(\frac{-A}{B} \right) \right]$$
(10)

where,
$$C = \tan^{-1}\left(\frac{1-A}{B}\right) - \tan^{-1}\left(\frac{-A}{B}\right)$$
, $A = \exp\left(A_0 + \frac{A_1}{T}\right)$ is the locus of the maximum of the

distribution function in terms of relative humidity. So, the adsorption uptake depends on three parameters A_0, A_1, B and saturation uptake W_s [g/g].

2.9. Brunauer-Emmet-Teller (BET) Model

The Brunauer–Emmet–Teller (BET) model is developed to explain multilayer adsorption and is most widely used in the characterization of porous materials. The assumptions of the theory are the same as those used in Langmuir's theory. It is assumed that the interaction energy between solid and molecule of the first layer is higher than the heat of vaporization. The heat of adsorption of the second and subsequent layers are the same and equal to the heat of liquefaction [45]. The BET model is given by,

$$\frac{V}{V_{m}} = \frac{Cx}{(1-x)(1-x+Cx)}$$
(11)

where *x* is the pressure ratio $x = \frac{P}{P_0}$, *V* is the amount of total gas adsorbed [m³], *V*_m is the monolayer coverage [nm]. The parameter *C* depends on the exponential of the difference between the adsorption energy of the first layer and the heat of liquefaction[–]. The larger the value of *C*, the sooner is the multilayer formation, and the convexity of the isotherm increases toward the low-pressure range.

2.10. Modified BET Model

The BET model is unable to explain the adsorption uptake near saturation pressure since with x = 1, and uptake becomes infinite. It assumes that adsorption heat of the second layer and the next several layers being less than the heat of liquefaction [45]. The model is thus modified by introducing a parameter K, and the modified model takes the form,

$$\frac{V}{V_m} = \frac{CKx}{(1 - Kx)\{(1 + (C - 1)Kx)\}}$$
(12)

If *K* = 1, the modified BET model becomes the classical BET model.

2.11. Guggenheim-Anderson-De Boer (GAB) Model

The Guggenheim–Anderson–De Boer (GAB) model [33] is also a modification of the BET model and is used for the fitting of type III adsorption isotherm. It can be described by,

$$\frac{V}{V_m} = \frac{CKx}{(1 - Kx)\{1 + (C - 1)Kx\}}$$
(13)

where, *C* and *K* are constant parameters related to the temperature of following equations, $C = C_0 \exp\left(\frac{\Delta H_1}{RT}\right)$ and $K = K_0 \exp\left(\frac{\Delta H_2}{RT}\right)$; and $\Delta H_1 = H_m - H_n$, $\Delta H_2 = H_1 - H_n$ are the functions of

the heat of adsorption. H_m and H_n are the heat of adsorption for monolayer and multilayer adsorption of water.

2.12. Sun and Chakraborty Model

Sun and Chakraborty [55] developed a model that can explain well the S-shaped isotherms. The model can thermodynamically connect the adsorption uptake with the porous structure of the adsorbent material. The uptake is a function of isosteric heat of adsorption and depends on the adsorptive sites of the adsorbent materials. The model can be expressed by,

$$\frac{W}{W_0} = \frac{K\left(\frac{P}{P_s}\right)^m}{1 + (K-1)\left(\frac{P}{P_s}\right)^m}$$
(14)

where $K = \alpha \exp \left[\frac{m(Q - h_{fg})}{RT} \right]$. *Q* is the isosteric heat of adsorption at zero surface coverage

[kJ/kg], and h_{fg} is the enthalpy of evaporation [kJ/kg].

2.13. Hybrid Model (Henry + Sips)

The hybrid model proposed by Kim et al. [38] comprising both the Henry and Sips isotherms includes nine parameters that are physically meaningful. The hybrid model is expressed as,

$$q = \beta K_{H} \left(\frac{P}{P_{s}}\right) + (1 - \beta) \frac{q_{m} \left(K_{s} P / P_{s}\right)^{1/n}}{1 + \left(K_{s} P / P_{s}\right)^{1/n}}$$
(15)

where q and q^m denote the absolute and maximum amount adsorbed. *n* is the heterogeneity parameter determined by $n = A + \frac{B}{T}$. *A* and *B* are the parameters of heterogeneity $\beta = \exp\left(-\alpha \frac{P}{P_s}\right)$, where α is a function of temperature following relation $\alpha = K_1 + K_2 \frac{T}{T_{ref}}$. The reference temperature $T_{ref} = 273.15 \ K$. The first term of the right- hand side of the Equation (15) is dominant in the low pressure or Henry region, and the last term takes dominance in the high-pressure region. *K* is the Henry constant whose values for both the regions are determined from $K = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$, where K_0 is the pre-exponential factor of the Henry constant, and ΔH is the isosteric enthalpy of adsorption at zero loadings.

2.14. Ben Yahia Model

The mathematical model developed by Yahia et al. [42], is used for the fitting of the Type-VI adsorption isotherm. They inferred that there could be two possibilities to explain the shape of this curve: energetic and geometric/stereographic. According to their assumptions, the energetic aspect is dominant, and there are four levels of energy present in the adsorption surface. The equation to determine the adsorbed quantity at equilibrium is expressed as,

$$W = \frac{n_1 N_{M1} \left(\frac{P}{P_1}\right)^{n_1}}{1 + \left(\frac{P}{P_1}\right)^{n_1}} + \frac{n_2 N_{M2} \left(\frac{P}{P_2}\right)^{n_2}}{1 + \left(\frac{P}{P_2}\right)^{n_2^2}} + \frac{n_3 N_{M3} \left(\frac{P}{P_3}\right)^{n_3}}{1 + \left(\frac{P}{P_3}\right)^{n_3^3}} + \frac{n_4 N_{M4} \left(\frac{P}{P_4}\right)^{n_4}}{1 + \left(\frac{P}{P_4}\right)^{n_4^4}}$$
(16)

with *i* = 1, 2, 3, and 4, pressure P_i can be expressed as, $P_i = P_s \exp\left(\frac{E_{ai}}{RT}\right)$. *n*_i is the number of molecules per site, N_{mi} is the density of receptor sites, and E_{ai} denotes the molar adsorption energy of gases in the site *i*.

2.15. Universal Isotherm Model

A universal isotherm model is proposed by Ng et al. [41], which assumed adsorbent with the heterogeneous surface where homogeneity is assumed in each site for energy level and which can be expressed by,

$$\frac{q}{q^*} = \sum_{i=1}^n \alpha_i \left[\frac{\left(\frac{p}{p_s} \exp\left(\frac{\varepsilon_{oi}}{RT}\right)\right)^{\frac{RT}{mi}}}{1 + \left(\frac{p}{p_s} \exp\left(\frac{\varepsilon_{oi}}{RT}\right)\right)^{\frac{RT}{mi}}}\right]_i$$
(17)

where, n = 2 indicates that two peaks can describe the energy distribution of the isotherm, which is valid for IUPAC classified isotherms from Type-I to Type-V having varied probability factors α_1 and α_2 where $\alpha_1 + \alpha_2 = 1$. For Type-VI, the energy distribution function needs four peaks (n = 4) with probability factors α_1 , α_2 , α_3 , and α_4 , where $\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1$. ε_{oi} is the adsorption energy site with maximum frequency and m_i denotes the range of energy sites available for adsorption. In other words, they represent the mean and deviation of an energy term, respectively. The larger value of m means high surface heterogeneity as well as the smaller slope of the model graph.

3. Error Evaluation Function

In this study, two error functions, namely the HYBRID and RMSD error functions, are used to optimize the parameters of the models. In our previous study [21], through analysis of the sum of normalized error (SNE), it was concluded that the HYBRID error function is appropriate to use for parameter optimization for almost all isotherm models. On the other hand, RMSD error function is frequently used by the researchers [21] for the optimization of parameters. Simultaneous use of these two error functions is considered in the current study for optimization since both of them are squared-type error function.

3.1. Root Mean Square Deviation (RMSD)

The most widely used error function used by the researchers is RMSD, which can be expressed as,

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n} \left(W_{experimental} - W_{calculated}\right)_{i}^{2}}{n}}$$
(18)

RMSD error function is used to estimate the parameters of the model, avoiding large error deviation between experimental data and the isotherm model. The error distribution of RMSD follows meso-kurtic, which is the assumption of least square regression fitting.

3.2. Hybrid Fractional Error Deviation (HYBRID)

Assumptions of RMSD/SSE errors are unbiased, free from outliers, and errors follow normal distribution [56]. Some special cases do not follow these assumptions. For example, in a low-pressure region, experimental uptake is not found precisely. In this case, some errors (deviation from the model) are considered as outliers. On the other hand, if we increase the model parameters, better fitting is possible. However, it will increase the model complexity. So the effect of the number of parameters should be incorporated in the error evaluation function. Porter et al. [57] developed a new error evaluation function, known as hybrid error evaluation function and denoted by HYBRID in the current study, for improving the fit of low- pressure region. In the HYBRID error function, the parameter effect is considered. This HYBRID error evaluation function balances absolute deviation against fractional error. It can be expressed as,

$$HYBRID = \frac{100}{n-p} * \sum_{i=1}^{n} \left[\frac{\left(W_{calculated} - W_{experimental}} \right)^2}{W_{experimental}} \right]_i$$
(19)

Here, *p* is the number of parameters in the model, and (n - p) is the degrees of freedom. HYBRID error evaluation function considers the number of parameters in the model. So, for the comparison of several models with an unequal number of parameters, the HYBRID error evaluation function is found to be more suitable than the RMSD error function.

4. Statistical Tools

In this section, we introduce the statistical techniques applied for selecting the best model(s) for the eight IUPAC-classified types of isotherms. These models are compared based on a number of model selection criteria discussed in Section 4.1. The selection criteria require estimating the residual sum of squares (RSS) for the candidate models, i.e., the sum of the squared differences between the observed and expected values of Y (uptake). However, given the model under study, the experimental data allows obtaining a single estimate of RSS, which in turn gives an estimate for each of the selection criteria. For deterministic (mathematical) models, one approach to drawing inference on the likelihood of selecting a model can be based on simulation studies (non-parametric methods). In the present context, a simulation-based approach generates samples repeatedly from the exiting data, since the actual experiment cannot be repeated many times due to time and economic constraints. We consider the bootstrap sampling approach (Section 4.2) for generating the repeated samples. Since our experiment was conducted under controlled conditions, the experimental outcomes are assumed to represent the underlying (non-existent) population. Thus, the simulated data are also assumed to represent the actual outcome for the corresponding treatment combinations. This allows comparing the candidate models a large number of times by estimating a selection criterion from each sample. The proportion of samples that correspond to a certain model having the minimum of a selection criterion among the candidate models gives an empirical estimate of the rate (likelihood) that the model is selected by the criterion for such experimental outcomes as in the current study. In this study, the likelihood of each model is estimated separately for each criterion, and statistical tests are carried out for finding evidence that certain model(s) may be more likely to be selected (better) than other models. The statistical tests include the overall proportion test and pairwise comparisons discussed in Section 4.3.

4.1. Information-Based Criterion for Model Selection

Given a dataset and a list of candidate models, one approach to selecting the best model is by estimating a model selection criterion. The commonly used criteria in the literature include the AIC, BIC, and their extensions, which are called the information-based criteria (IC). The IC estimates a loss of information that the model incurs, as a measure of distance from the most parsimonious (true) model. Thus, the model with the lowest IC incurs the minimum information loss, hence selected as the parsimonious to the true model. In this study, a number of information criteria are applied separately for selecting the best candidate model among the candidates.

The information-based criteria consist of the goodness of fit term (maximized log-likelihood, -2l) and a penalty term f(n,p) for the complexity of the model. The penalty term f(n,p) is a function of sample size (*n*) and the number of parameters (*p*), required for fitting the model [58–60]. Under Gaussian error, the term -2l can be expressed as $n(log(2\pi) + log(RSS) + log(n) + 1)$, which indicates that for fixed *n*, the goodness of fit term is mainly a function of residual sum of squares. In general, the information-based model selection criteria take the form

$$IC = -2l + f(n, p) \tag{20}$$

Akaika (1969) [61–63] proposed using f(n,p) = 2p and suggests that the criterion AIC = -2l + 2p[59] minimizes the average Kulback–Leibler (K–L) distance (1951) [64] between the candidate model and the true model. It was found that the performances of AIC were poor if the number of parameters in the model is large compared to the sample size [60]. Considering the K–L distance and maximized log-likelihood, different authors [65–67] recommended using corrected versions of AIC, which usually apply a slightly heavier penalty to the goodness of fit term. Sugiura [66] first derived a second-order alternative of *AIC* in which bias correction was added by Hurvich and Tsai [65]. Thus, a corrected version of AIC namely, AICc. If n is large, compared to p, the correction terms [n/(n - p - p)]1)] is negligible; hence, the AICc and AIC are equally efficient. In all other cases, it is recommended to use AICc [68]. Phoa et al. [69] recommended a modified version of AIC, i.e., $mAIC = -2l + 2p^2$, which uses a quadratic penalty for model complexity instead of a linear penalty in AIC. In a Bayesian framework, Schwarz (1978) [70] proposed BIC = -2l + pln(n) [70] that uses Bayesian information and posterior probability. The form of *BIC* is similar to *AIC* except that the penalty term 2p is replaced by pln(n). Sclove (1987) [58] proposed adjusted BIC (denoted by ABIC), based on the information from Rissanen (1978) [71] and Boekee and Buss (1981) [72]. Here, the form of the penalty term is, f(n,p) =pln[(n + 2)/24] [21,48]. Likewise, Bozdogan [62] proposed another modified version of BIC, namely *CAIC* using f(n,p) = p[ln(n) + 1). More explanation of information-based criteria can be found in our previous study [21]. In this paper, the information criterion (IC) as mentioned above is applied separately for comparing the selection rates of the competing models. Since current experimental outputs allow only one estimate of each criterion for the competing models, we consider bootstrap samples to re-estimate the criteria many times and compared the likelihood of the models, separately for each criterion. Therefore, we have concluded our findings based on the decision of the majority of the ICs.

4.2. Bootstrap Approach

Efron and Tibshi-rani (1993) [73] introduced a bootstrap sampling method that can be used to perform data-based (non-parametric) statistical inference [74]. In this approach, the observed/experimental data are assumed to represent the underlying population, and new samples are generated by randomly selecting samples from the original sample (outcome) with replacement. Thus, an estimate of a parameter/metric or a hypothesis test can be obtained repeatedly based on random samples of the same size as the original sample. The estimates from the repeated samples generate an empirical sampling distribution as a straightforward non-parametric way to derive the standard errors and confidence intervals of complex parameters, such as percentile points, proportions, odds ratio, and correlation coefficients. In the present context, the parameter of interest is the residual sum of squares of the candidate models. The underlying idea of bootstrapping is that the inference about a population from sample data (sample \rightarrow population) can be modeled by resampling the sample data and performing inference about a sample from resampled data (resampled \rightarrow sample).

In the context of the present study, the outcome of the experiments is the base sample, from which the observed estimates of RMSD/HYBRID (and the IC) for the candidate models. In practice, since it is usually not feasible to repeat an experiment large number of times, bootstrapping allows generating a large number of samples, so that the errors can be estimated repeatedly from these data sets. Here the *i*-th bootstrap sample (i = 1, 2, ..., L) gives the *i*-th estimate of observed error, the RSSi (i = 1, 2, ..., L) for the goodness of fit terms, which in turn is used to estimate the IC. In this study, L = 1000 is used as we believe that the number is large enough to generate the sampling distributions of the estimates. Using these bootstrap estimates, we thus test for significance of RSS and obtain interval estimates in a nonparametric approach.

4.3. Bootstrap p-Value and Confidence Interval (CI) of Residual Sum of Squares (RSS)

The bootstrap distribution of error allows finding the *p*-value and confidence interval of RSS. The confidence interval [56] gives a degree of certainty of an estimator since it is associated with a probability statement. If the same sampling technique is employed to draw different samples and 95% confidence interval is calculated, then the probability that the true parameter will fall in that interval is 0.95. In this study, the 95% bootstrap confidence intervals (CIs) for the errors are obtained by discarding the 2.5% lower and 2.5% higher values of observed errors from the bootstrap distribution. The tail area in bootstrap distribution, starting from the observed RSS, gives *p*-value [21] for testing the significance of the error estimate.

Thus in a bootstrap approach, *p*-value refers to the proportion of bootstrap samples that correspond to the observed and more extreme values of observed error.

4.4. Proportion Tests

The bootstrap samples generate 1000 estimates of each IC, separately for each candidate model. For a certain criterion, the proportion of 1000 samples when a model archives the minimum value compared to other candidate models, is given by:

(Number of times the model attains minimum IC)/(1000 (number of bootstrap samples))

Using the bootstrap samples, since we estimate each IC separately for six (for example) candidate models, the models correspond to six proportions for a given criterion. The proportions are estimated rate or likelihood that the models are selected by the specific criterion. Since the proportions are bootstrap estimates of true likelihood, we perform a statistical test for the equality of the likelihoods.

Hypotheses (H0). The models are equally likely to be selected by the criterion.

vs.

Hypotheses (H1). They are not equally likely

A rejection of the hypothesis leads to pairwise comparisons of the proportions. These tests are conducted by applying a chi-square test and t-tests, respectively. Thus, a single or set of best models are identified SEPARATELY by each criterion.

4.4.1. Chi-Squared Test for Equality of Proportions

The Chi-squared test is an overall test for the equality of more than two proportions. For example, suppose a gambler wishes to test if the six numbers of a six-sided die are equally likely to appear on the top when the die is rolled. The gambler performs an experiment by rolling the die a large number (say 1000) of times and records the frequency (Oi) that the *i*-th number (*i* = 1,2,...,6) appears on top out of the 1000 trials. Thus, the proportion $\hat{\pi} = \frac{O_i}{1000}$. If P₁, P₂, ..., P₆ denote the actual probability of occurrence of the six numbers, then the following hypotheses can be tested by applying the chi-squared test,

Hypotheses (H0). $P_1 = P_2 = ... = P_6$ vs.

Hypotheses (H1). At least two are different

The test-statistic is given by,

$$\chi^{2} = \sum_{i=1}^{6} \frac{(O_{i} - E_{i})^{2}}{E_{i}}$$

where O_i refers to the observed frequency and $E_i = (1/6)$, *L refers to the expected frequency of i-th number in the 1000 trials under the assumption that H_0 is true. The test statistic is chi-square distribution with 5 degrees of freedom. The overall proportion test rejects H_0 in favor of H_1 if the *p*-value is less than the significance level $\alpha = 0.05$.

As with the above example, in this study, we have six candidate models. For each bootstrap sample, errors are obtained for different models; IC's are calculated based on the errors, and the model that attains the minimum of an IC is recorded. Given IC, thus, the *L* bootstrap samples give O_i and $E_i = (1/6) \times 1000$ for the i-th model (i = 1, 2, ..., 6). Finally, the test statistic is calculated, and the *p*-value is obtained. A small *p*-value (<0.05) is a piece of evidence against the hypothesis that the six-candidate models are equally likely to be selected by the criterion. This indicates that the proportions of times the models attained minimum IC may not be equal. In other words, at least one model may be more likely to be selected by the criterion compared to other models when *p*-value

<0.05. The overall test is conducted separately for each criterion to examine if certain model(s) consistently attain a higher chance to be selected by most criteria.

4.4.2. Pairwise Test: Multiple Comparisons

In case the overall proportion test shows evidence against equality of likelihoods of the six models, it is of interest to identify which model(s) may have a relatively higher chance of to be selected by an IC. This is done by multiple comparisons tests [75], which performs pairwise comparisons of all ${}^{6}C_{2} = 15$ pairs of proportions. For example, the hypothesis that model 1 and model 2 are equally likely to attain a minimum value of a given IC (i.e., equally likely to be selected) is denoted as follows.

$$H_0: P_1 = P_2$$
 Vs. $H_0: P_1 \neq P_2$

*H*₀ is rejected at 5% level of significance if the test statistic $Z = \frac{\hat{p}_1 - \hat{p}_2}{\sqrt{\hat{p}(1-\hat{p})\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$, where $\hat{p} = \frac{x_1 + x_2}{n_1 + n_2}$ results the *p*-value < 0.05. By rejecting *H*₀, the pair-wise test suggests that one model may

be more likely to be selected by a given IC than the other model. In such a case, the model that attains a higher $\hat{\pi}$ value can be declared to be the better model. Similarly, all other pairs of models are compared based on certain model selection criteria, and finally, a single or set of model(s) are identified that may be better than the other candidates. In this study, since we consider eight different criteria, the overall test and multiple comparisons are conducted separately for each criterion.

5. Results and Discussion

In this study, relevant adsorption pairs for all the IUPAC-classified adsorption isotherms are first selected for analysis. One adsorption pair data with more than one temperature consider for Type-I(b), Type-III, and Type-V. On the other hand, two different adsorption pairs with single temperature consider for Type-I(a), Type-II, Type-IV(a), Type-IV(b) and Type-VI IUPAC classified adsorption isotherm. Generalized reduced gradient (GRG) non-linear optimization methods have been employed to optimize the parameters of the model using two error evaluation functions RMSD and HYBRID for Type-I(a) and Type-I(b) adsorption isotherm. On the other hand, the only HYBRID error evaluation function is used for other types since Rahman et al. [21] showed that HYBRID error was better than other errors for the optimization of parameters. Bootstrap error mean, CI, the value of model selection criteria, selection probabilities/rates of the model have been calculated, and two proportion tests have been performed for Type-I(a), Type-I(b), Type-III, and Type-V adsorption isotherms. For Type-II, Type-IV(a), Type-IV(b) and Type-VI, the bootstrap error means, CI, the value of model selection criteria have been presented.

5.1. Type-I(a) Adsorption Isotherm

Type-I(a) is recommended isotherm in the 2015 IUPAC report [14]. This type of isotherm is found for narrow microporous adsorbent having a pore size less than 1 nm. For instance, adsorption of N2 onto K4-700 adsorbent at temperature 77 K [18] and Ar onto BIDC-X-700 adsorbent at temperature 87 K [19] showed Type-I(a) isotherm.

5.1.1. Bootstrap Error Analysis and Model Selection Using Information Criteria

Hu et al. [18] measured the adsorption isotherms at 77 K for adsorption of high-resolution N_2 onto a K4-700. Cychosz et al. [19] measured adsorption isotherm at 87 K for adsorption of argon onto heteroatom-doped carbons BIDC-X-700 adsorbent. These isotherms are fitted with Tóth, D-A, Mod-BET, Ng et al., and Mahle model in the current study and presented in Figure 2.

Based on the bootstrap mean and CIs of the RMSD and HYBRID errors from Table 2, it is observed that the modified BET model has smaller average error and smaller CI than the other models.

The value of all information criteria in the bold number of modified BET model is small compared to other probable model for carbon K4-700/N₂ and BIDC-1-700/Ar adsorption pairs presented in Table 3, which means that considering all ICs and both error functions, modified BET models information loss is less compared to other models followed by the Tóth model. The probability of the possible models for Type-I(a) is graphically presented in Figure 3. It is marked that the selection rate/probability of the modified BET model is maximum among all the models considering all criteria for both adsorption pairs.



Figure 2. Type-I(a) adsorption isotherm of Carbon K4-700/N₂ and BIDC-1-700/Ar pairs (data are fitted with the D–A, Tóth, modified BET, Ng et al. and Mahle models using RMSD and HYBRID error evaluation functions) depicted in (**a**) and (**b**), respectively.

Model	Mean RMSD	CI of RMSD	Mean HYBRID	CI of HYBRID
K4-700/N ₂	pair			
Tóth	0.0745	(0.045, 0.0956)	1.884	(1.24, 2.152)
D-A	0.0838	(0.047, 0.0971)	1.912	(1.55, 2.923)
Mod. BET	0.0638	(0.050, 0.0723)	1.871	(1.52, 1.983)
Ng et al.	0.1066	(0.032, 0.3254)	1.913	(1.43, 3.851)
Mahle	0.1019	(0.042, 0.2321)	4.146	(3.654, 5.123)
BIDC-1-700)/Ar pair			
Tóth	0.1047	(0.045, 0.126)	3.6648	(2.24, 4.152)
D-A	0.0936	(0.047, 0.0971)	8.9234	(6.55, 10.923)
Mod. BET	0.0872	(0.050, 0.0986)	3.5624	(2.52, 4.783)
Ng et al.	0.1245	(0.032, 0.3254)	12.354	(8.43, 15.851)
Mahle	0.1154	(0.042, 0.2921)	4.8132	(2.65, 7.123)

Table 2. Mean error and confidence interval of error for n = 1000 bootstrap samples for K4-700/N₂ and BIDC-1-700/Ar pairs.

Table 3. Optimal isotherm employing model selection criteria for n = 1000 bootstrap samples for K4-700/N₂ and BIDC-1-700/Ar pair.

Model	Error Mean	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC	
K4-700/N ₂	pair								
Using RMSD error mean									
Tóth	0.0745	-223.16	-214.78	-222.43	-199.16	-219.16	-210.78	-227.36	
D-A	0.0838	-218.08	-211.79	-217.65	-206.08	-215.08	-208.79	-221.23	
Mod. BET	0.0638	-234.48	-228.20	-234.06	-222.48	-231.48	-225.20	-237.64	
Ng et al.	0.1066	-195.68	-181.02	-193.53	-111.68	-188.68	-174.02	-203.04	
Mahle	0.1019	-204.38	-196.00	-203.65	-180.38	-200.38	-192.00	-208.58	
		Us	sing HYBI	RID error i	mean				
Tóth	1.884	-29.33	-20.96	-28.61	-5.33	-25.33	-16.96	-33.54	
D-A	1.912	-30.47	-24.19	-30.05	-18.47	-27.47	-21.19	-33.63	
Mod. BET	1.871	-31.78	-25.49	-31.35	-19.78	-28.78	-22.49	-34.93	
Ng et al.	1.913	-22.44	-7.78	-20.29	61.56	-15.44	-0.78	-29.80	
Mahle	4.146	17.96	26.34	18.69	41.96	21.96	30.34	13.76	
BIDC-1-700)/Ar pair								
		ι	Jsing RMS	SD error m	nean				
Tóth	0.1047	-69.02	-63.69	-67.28	-45.02	-65.02	-59.69	-76.12	
D-A	0.0936	-74.15	-70.16	-73.15	-62.15	-71.15	-67.16	-79.48	
Mod. BET	0.0872	-76.14	-72.14	-75.14	-64.14	-73.14	-69.14	-81.47	
Ng et al.	0.1245	-58.17	-48.84	-52.57	25.83	-51.17	-41.84	-70.60	
Mahle	0.1154	-66.29	-60.96	-64.55	-42.29	-62.29	-56.96	-73.40	
		Us	sing HYBI	RID error i	mean				
Tóth	3.6648	30.54	35.86	32.27	54.54	34.54	39.86	23.43	
D-A	8.9234	53.45	57.45	54.45	65.45	56.45	60.45	48.12	
Mod. BET	3.5624	27.74	31.74	28.74	39.74	30.74	34.74	22.41	
Ng et al.	12.354	70.56	79.89	76.16	154.56	77.56	86.89	58.12	
Mahle	4.8132	38.17	43.50	39.91	62.17	42.17	47.50	31.06	



Figure 3. Probability/rate of selecting models for K4-700/N₂ and BDIC-1-700/Ar of Type-I(a) adsorption isotherms using both RMSD and HYBRID errors depicted in (**a**) and (**b**), respectively.

5.1.2. Overall and Pairwise Proportion Tests

The *p*-values of overall and pairwise tests for the equality of minimum information criteria for carbon K4-700/N₂ and BIDC-1-700/Ar pairs considering three more important models are expressed in Table 4. Here, the *p*-value of two tests are given, (i) equality of overall (all models) proportion test and (ii) equality of pairwise proportion test. For K4-700/N₂ pairs, Table 4 shows that *p*-value is very small, which is close to zero and less than 0.01. Thus, it indicates that the overall and pairwise proportion tests are highly statistically significant at 1% level of significance. It states that the Mod. BET model has significantly less information loss compare to other probable models. For BIDC-1-700/Ar pairs, Table 4 shows that *p*-value is very small, which is close to zero and less than 0.01 except pairwise test between modified BET and Tóth model. Thus, it indicates that the overall

and pairwise (Mod. BET vs. D–A) proportion tests are statistically significant at 1% level of significance, but modified BET and Tóth is insignificant. It states that the Mod. BET and Tóth model are equally important for Type-I(a).

Table 4. *p*-value of the overall and pairwise test of equality of the values of minimum information criteria (Values outside and inside of parentheses represent HYBRID and RMSD errors, respectively) for carbon K4-700/N₂ and BIDC-1-700/Ar pairs.

Test	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Carbon K4	-700/N2						
	2.0×10^{-15}	2.1 × 10-	2.2×10^{-15}	2.0×10^{-13}	2.1×10^{-15}	2.0×10^{-14}	2.1×10^{-15}
Overall	(2.3 × 10−	(2.1 × 10−	(2.0 × 10-	(2.2 × 10-	(2.2 × 10−	(2.2 × 10-	(2.2 × 10−
	¹⁴)	¹³)	¹⁴)	¹²)	¹³)	¹⁴)	¹³)
Mod. BET vs. Tóth	2.0 × 10-4 (2.1 × 10-5)	2.1 × 10 ⁻⁵ (2.0 × 10 ⁻⁴)	2.2 × 10 ⁻³ (2.1 × 10 ⁻⁴)	1.4 × 10− (1.2 × 10-3)	1.8 × 10 ⁻⁴ (2.1 × 10 ⁻³)	1.9 × 10-³ (2.1 × 10−³)	2.1 × 10 ⁻⁴ (2.2 × 10 ⁻³)
Mod. BET vs. D–A	1.5 × 10 ⁻⁸ (1.9 × 10 ⁻⁸)	2.1 × 10 ⁻⁹ (2.0 × 10 ⁻⁷)	1.1 × 10 ⁻⁸ (2.1 × 10 ⁻⁸)	2.0 × 10 ⁻⁷ (2.0 × 10 ⁻⁷)	2.0 × 10 ⁻⁸ (1.9 × 10 ⁻⁷)	1.7 × 10 ⁻⁹ (2.2 × 10 ⁻⁹)	2.1×10^{-11} (1.9 × 10 ⁻¹²)
BIDC-1-700	0/Ar pair						
Overall	2.0×10^{-4} (2.3 × 10^{-3})	2.2 × 10 ⁻³ (2.1 × 10 ⁻³)	2.1×10^{-4} (2.3 × 10 ⁻³)	2.4 × 10 ⁻³ (2.1 × 10 ⁻⁴)	2.1×10^{-4} (2.3 × 10 ⁻⁵)	2.5 × 10 ⁻³ (2.1 × 10 ⁻⁴)	2.2 × 10 ⁻⁴ (2.3 × 10 ⁻³)
Mod. BET vs. Tóth	0.0235 (0.0351)	0.0351 (0.0421)	0.2363 (0.5324)	0.0425 (0.0354)	0.0573 (0.0784)	0.2381 (0.1465)	0.0715 (0.0471)
Mod. BET vs. D-A	1.6× 10-3 (1.7× 10-4)	1.1 × 10-4 (2.4 × 10-3)	1.5 × 10 ⁻³ (2.3 × 10 ⁻³)	1.4 × 10 ⁻⁴ (2.2 × 10 ⁻³)	2.2 × 10 ⁻³ (1.5 × 10 ⁻⁴)	1.9 × 10-4 (2.1 × 10-3)	2.2 × 10 ⁻³ (1.44)

5.2. Type-I(b) Adsorption Isotherm

The Type-I(b) IUPAC [15,41] classified adsorption isotherm is mainly characterized by monolayer adsorption. The uptake continuously increases with pressure and reaches a plateau at saturation pressure. The maximum absorption is determined by the available micropore volume.

5.2.1. Bootstrap Error Analysis and Model Selection Using Information Criteria

Pal et al. [22] assessed the adsorption isotherms for adsorption of carbon-based composites onto carbon dioxide gas. They considered temperatures 30 °C, 50 °C and 70 °C. The isotherms are fitted with Tóth and modified D–A, Langmuir, Freundlich, D–A, and Hill model in the current study and presented in Figure 4. Applying bootstrap error analysis, for each type of isotherm, RMSD, HYBRID error mean, and CI of errors are measured. The results are presented in Table 5. It shows the mean RMSD and HYBRID errors as well as 95% confidence interval of the two, corresponding to all the isotherm models. It is observed that the Tóth model provides the minimum error and minimum 95% CI of the bootstrap sample compared to the other models.



Figure 4. Type-I(b) adsorption isotherm of carbon-based composite/CO₂ pair (data are fitted with the Tóth, modified D–A, Langmuir, Freundlich, and Hill models using RMSD and HYBRID error evaluation function, depicted in (**a**) and (**b**), respectively).

Table 5. Mean error and confidence interval of error for n = 1000 bootstrap samples.

Model	Mean RMSD	CI of RMSD	Mean HYBRID	CI of HYBRID
D–A	0.05624	(0.0457, 0.0650)	0.4893	(0.3432, 0.6382)
Mod. D–A	0.01532	(0.0125, 0.0179)	0.1096	(0.0745, 0.1438)
Tóth	0.01435	(0.0122, 0.0165)	0.0373	(0.0276, 0.0473)
Freundlich	0.05178	(0.0451, 0.0583)	0.4353	(0.3282, 0.5444)
Langmuir	0.01839	(0.0157, 0.0209)	0.0724	(0.0516, 0.0960)
Hill	0.04871	(0.0451, 0.0583)	0.3816	(0.2740, 0.4965)

From Table 6, it is observed that for the composite/CO₂ adsorption pair, the values of all information criteria for Tóth model are small compared to other probable models, considering HYBRID error mean; this implies that considering all IC, the Tóth model's information loss is less when compared to other models. The results are similar in the case of RMSD error mean; i.e., the values of all information criteria that correspond to the Tóth model are small compared to other probable models, except with the case of mAIC, which attains the minimum value in Langmuir model. Thus the analysis shows that, for this type of isotherm, the Tóth model's information loss is less compared to other models. The probability of the possible model for Type-I(b) is graphically presented in Figure 5. This bar diagram shows the selection probability of the models for each of the model selection criteria. It is evident that the selection rate/probability of the Tóth model is highest among all the models considering all criteria. According to *AIC*, using the RMSD error function, the selection probability of the Tóth model is approximately 70%. On the other hand, if we use the HYBRID error function, the selection probability of the Tóth model is about 80%.

Model	Error Mean	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC		
Using HYBRID error mean										
D-A	0.4893	-56.61	-51.70	-55.90	-44.61	-53.61	-48.70	-61.08		
Mod. D-A	0.1096	-114.43	-107.88	-113.22	-90.43	-110.43	-103.88	-120.38		
Tóth	0.0373	-157.53	-150.98	-156.32	-133.53	-153.53	-146.98	-163.49		
Freundlich	0.4353	-63.29	-60.01	-62.95	-59.29	-61.29	-58.01	-66.27		
Langmuir	0.0724	-133.03	-128.11	-132.32	-121.03	-130.03	-125.11	-137.50		
Hill	0.3815	-66.56	-61.65	-65.85	-54.56	-63.56	-58.65	-71.03		
		Us	ing RMS	D error m	ean					
D-A	0.0562	-143.15	-138.24	-142.44	-131.15	-140.15	-135.24	-147.62		
Mod. D-A	0.0153	-193.17	-186.62	-191.96	-169.17	-189.17	-182.62	-199.12		
Tóth	0.0143	-195.78	-189.23	-194.57	-171.78	-191.78	-185.23	-201.74		
Freundlich	0.0517	-148.45	-145.18	-148.11	-144.45	-146.45	-143.18	-151.43		
Langmuir	0.0183	-187.86	-182.95	-187.16	-175.86	-184.86	-179.95	-192.33		
Hill	0.0487	-148.90	-143.99	-148.19	-136.90	-145.90	-140.99	-153.37		

Table 6. Optimal isotherm employing model selection criteria for *n* = 1000 bootstrap samples.

* The shaded cells indicate lowest value for a particular information criterion.



Figure 5. Probability/rate of selecting models for Type-I(b) adsorption isotherms using both RMSD and HYBRID errors.

5.2.2. Overall and Pairwise Proportion Tests

p-value of overall and pairwise test for the equality of minimum information criteria considering Tóth, modified D–A, and Langmuir models are expressed in Table 7. Here, the *p*-value of two tests are given, (i) equality of overall (all models) proportion test and (ii) equality of pairwise proportion test. The above table shows that *p*-value is very small, which is close to zero and less than 0.01. Thus, it indicates that the overall and pairwise proportion tests are highly statistically significant at 1% level of significance. It states that the Tóth model has significantly less information loss compared to other probable models.

				1		· 1	57
Test	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Overall	2.1×10^{-16} (2.2 × 10 ⁻¹²)	2.1 × 10- ¹⁵ (2.2 × 10- ¹³)	2.1×10^{-16} (2.2 × 10 ⁻¹⁴)	2.2 × 10 ⁻¹⁴ (2.2 × 10 ⁻ ¹³)	2.2×10^{-16} (2.2 × 10 ⁻¹⁴)	2.0×10^{-13} (2.2 × 10 ⁻¹⁶)	2.2 × 10 ⁻¹⁶ (2.2 × 10 ⁻ ¹⁵)
Tóth vs. Mod. D–A	2.0 × 10- ¹² (2.0 × 10 ⁻¹⁶)	2.0 × 10- ¹¹ (2.0 × 10 ⁻¹⁶)	2.0×10^{-11} (2.0 × 10 ⁻¹⁶)	1.0×10^{-10} (1.0 × 10 ⁻¹⁰)	2.0×10^{-13} (2.0 × 10 ⁻¹⁶)	2.1 × 10 ⁻¹² (2.0 × 10 ⁻ ¹⁶)	2.0×10^{-13} (2.0 × 10 ⁻¹⁶)
Mod.D–A vs. Langmuir	1.9 × 10- ¹⁵ (2.0 × 10-16)	2.0 × 10 ⁻ ¹⁶ (2.0 × 10 ⁻¹⁶)	2.1×10^{-15} (2.0 × 10 ⁻¹⁶)	2.0×10^{-16} (2.0 × 10 ⁻¹⁶)	2.0×10^{-16} (2.0 × 10 ⁻¹⁶)	2.0×10^{-16} (2.0 × 10 ⁻¹⁶)	2.0×10^{-16} (2.0 × 10 ⁻¹⁶)

Table 7. *p*-value of the overall and pairwise test of equality of the values of minimum information criteria (values outside and inside of parentheses represent HYBRID and RMSD errors, respectively).

5.3. Type-II Adsorption Isotherm

The Type-II isotherm is characterized by multilayer adsorption [15] and nearly analogous to the Type-I(b) shape; the only difference between the two is the absence of the plateau in Type-II, which is observed in Type-I(b) isotherms. The uptake continuously increases even when the pressure ratio is close to unity. This type of behavior is found for microporous adsorbents. Two isotherm data, for Type-II, are analyzed in the current study, they are isotherms of (i) water adsorption onto alumina at 22 °C and (ii) water onto poorly crystalline boehmite at 20 °C. A previous study [21] on analysis of the sum of normalized error (SNE) showed that the HYBRID error function is appropriate to use for parameter optimization for almost all isotherm models. That is why the HYBRID error is used in the current study for the analysis of all types of onwards.

Naono et al. [31] determined the adsorption isotherms for adsorption of water onto alumina at 20 °C. Wang et al. [32] use water adsorption onto poorly crystalline boehmite at 22 °C. Both of these adsorption isotherms exhibit Type-II characteristics and are considered in the current study. The isotherm first fitted with modified BET, Ng et al., D–A, Tóth, Langmuir, and Redlich–Peterson models, and the fitted isotherms are represented in Figure 6. Bootstrap error analysis is performed, and the results of bootstrap error mean, and 95% CI are presented in Table 8.

Based on the bootstrap mean and CIs of the HYBRID errors, we observe that on average, the modified BET model has smaller errors and a minimum 95% confidence interval of bootstrap sample than the other models. The ICs of all the models is also determined in the current study and presented in Table 9. It is observed that all the information criteria corresponding to the modified BET model are smaller than the same corresponding to other isotherm models, and this statement is valid for both the adsorbate/adsorbent pairs. This signifies that the information loss in the case of the modified BET model is less than that corresponding to other isotherm models.



Figure 6. Type-II adsorption isotherms; (a) alumina/water pair and (b) poorly crystalline boehmite/water pair. Data are fitted with the modified BET, Ng et al., D–A, Toth, Langmuir, and Redlich–Peterson models using the HYBRID error evaluation function.

Table 8. Mean error and confidence interval of HYBRID error for $n = 1000$ bootstrap si	amples.
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Alu	mina/Water P	air	Boehmite/Water Pair				
Model	Mean error	95% CI of Error	Model	Mean Error	95% CI of Error		
Mod. BET	0.2739	(0.1476, 0.4204)	Mod. BET	0.0079	(0.0028, 0.0141)		
Ng et al.	0.8420	(0.3389, 1.5064)	Ng et al.	0.0311	(0.0121, 0.0588)		
D-A	1.0182	0.1739, 2.5075)	D-A	0.0357	(0.0132, 0.0743)		
Tóth	1.9345	(1.2436, 2.6768)	Tóth	0.6532	(0.2401, 1.2636)		
Redlich-Peterson	1.6072	(0.9935, 2.3879)	Langmuir	1.4360	(0.5127, 2.7516)		

Model	Mean Error	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Adsorption of water onto alumina								
Mod. BET	0.2739	-41.32	-37.44	-40.28	-29.32	-38.32	-34.44	-46.76
Ng et al.	0.8420	-3.00	6.07	2.89	81.00	4.00	13.07	-15.68
D-A	1.0182	-5.87	-1.98	-4.82	6.13	-2.87	1.02	-11.30
Tóth	1.9345	13.46	18.65	15.28	37.46	17.46	22.65	6.22
Redlich-Peterson	1.6072	8.46	13.64	10.28	32.46	12.46	17.64	1.21
	Adsorption	of water o	onto poor	ly crystall	line boeh	mite		
Mod. BET	0.0079	-70.43	-68.11	-68.43	-58.43	-67.43	-65.11	-77.30
Ng et al.	0.0311	-40.48	-35.07	-26.48	43.52	-33.48	-28.07	-56.50
D-A	0.0356	-46.31	-44.00	-44.31	-34.31	-43.31	-41.00	-53.18
Tóth	0.6532	2.24	5.33	5.87	26.24	6.24	9.33	-6.91
Langmuir	1.4359	12.84	15.16	14.84	24.84	15.84	18.16	5.98

Table 9. Optimal isotherm employing model selection criteria using HYBRID error mean of *n* = 1000 bootstrap samples.

5.4. Type-III Adsorption Isotherm

The shape of the Type-III adsorption isotherm is convex [15,41]. At low pressures, the uptake is low, but it increases sharply at the high pressures. Maroulis et al. [33] fitted the GAB model for the adsorption of moisture on the dried fruits. They considered temperatures of 15 °C, 30 °C, 45 °C and 60 °C. In the current study, these isotherms are fitted with GAB, modified BET, Ng et al., modified Langmuir, Sun and Chakraborty, and D–A models and the results are shown in Figure 7. To investigate the model selection bootstrap error mean, 95% CI of n = 1000 bootstrap sample and model selection criteria are determined and presented in Table 10. It is evident that considering all information criteria, the GAB model's information loss is less compared to all other models. Mean error and 95% confidence interval of bootstrap samples are also small when the GAB model is considered in the fitting.

Figure 8 shows the selection probability of three models for each criterion. The bar diagram indicates that the selection rate/probability of the GAB model for adsorption of moisture/dried raisin pair is more than 80%, whereas the modified BET model has a selection probability of 10% approximately for most of the information criteria except BIC and mAIC.

The overall and pairwise proportion tests are also conducted, and the results are presented in Table 11. It is observed that the *p*-value is very small and much less than 0.01. This result indicates that the overall and pairwise proportion tests are highly statistically significant. It also reconfirms that the GAB model has significantly less information loss compared to other models taken into consideration.



Figure 7. Type-III adsorption isotherms for dried raisins/moisture pair; experimental data are fitted with the GAB, modified BET, Ng et al., modified Langmuir, Sun and Chakraborty and D–A models using HYBRID error evaluation function.

Table 10. Optimal isotherm employing model selection criteria using HYBRID error mean of *n* = 1000 bootstrap samples.

Model	Mean Error	95% CI of Error	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
GAB model	0.2932	(0.1720, 0.4280)	-73.10	-64.66	-71.34	-33.10	-68.10	-59.66	-80.30
Mod. BET	0.8758	(0.3509, 1.5002)	-33.33	-28.26	-32.66	-21.33	-30.33	-25.26	-37.65
Ng et al.	1.0613	(0.6907, 1.4828)	-17.64	-5.82	-14.14	66.36	-10.64	1.18	-27.73
D-A	1.2565	(0.6192, 2.0008)	-18.89	-13.82	-18.22	-6.89	-15.89	-10.82	-23.21
Sun and Chakraborty	1.3858	(0.7615, 2.0736)	-12.97	-6.22	-11.83	11.03	-8.97	-2.22	-18.73
Mod. Langmuir	0.7541	(0.3423, 1.2238)	-31.31	-19.49	-27.81	52.69	-24.31	-12.49	-41.39



Figure 8. Probability of selecting models of Type-III adsorption isotherms for different information criteria using HYBRID errors.

Table 11. *p*-value of an overall and pairwise test of equality of the value of minimum IC using HYBRID error of n = 1000 bootstrap samples.

Test	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Overall	2.2 × 10-	2.2 × 10-	2.2 × 10-	2.2 × 10-	2.2 × 10-	2.2 × 10-	2.2×10^{-1}
Overall	16	16	16	16	16	16	16
CAD M. I DET	2.0 × 10-	2.0 × 10-	2.0 × 10-	2.0 × 10-	2.0 × 10-	2.0 × 10-	2.0 × 10-
GAB vs. Mod. BEI	14	13	14	12	15	14	14
GAB vs. Mod.	2.0×10^{-1}	2.0 × 10-	2.1 × 10-	2.2 × 10-	2.2 × 10-	2.0 × 10-	2.1 × 10-
Langmuir	15	15	14	15	15	15	15

5.5. Type-IV(a) Adsorption Isotherm

The Type-IV(a) IUPAC classified adsorption isotherm is described by multilayer adsorption, which is a combination of Type-I(b) and Type-II isotherms. This type is characterized by its hysteresis loop, caused by the filling of mesopores. In the present investigation, two isotherms data are considered; (i) water adsorption onto polyvinylidene chloride (PVDC-600 °C) at 35 °C and (ii) water onto tripolis (dispersed silica) at 21 °C. Do et al. [34] presented a model that can describe the behavior of water adsorption onto highly oxidized carbon at 35 °C. Rakitskaya et al. [35] fitted the BET model to describe the adsorption of water onto tripolis. In the current study, these isotherms are fitted with the Ng et al., Yahia et al., modified BET, Mahle, Sun and Chakraborty, and Do et al. models. Figure 9 shows the fitting of isotherm data for PVDC/water pair and Tripolis/water pair with different isotherm models using the HYBRID error evaluation function.

Mean HYBRID error and 95% confidence interval of errors are given in Table 12 for adsorption of water onto PVDC and water onto Tripolis pairs. The results indicate that mean error and 95% CI of the bootstrap samples are small for the Ng et al. model, as compared to other models. This statement is also checked by determining various information criteria, as presented in Table 13. It is observed that the values of all information criteria, except mAIC, of the Ng et al. model, are small compared to other probable models, for the adsorption of PVDC/water pair. Since the Ng et al. model is selected by the majority of the information criterion, so it signifies that considering IC the Ng et al. model's information loss is less when compared to other models, and the method mAIC is not appropriate in this case. A similar finding is obtained in the case of the adsorption of water onto tripolis.



Figure 9. Type-IV(a) adsorption isotherms for (a) PVDC/water pair and (b) Tripolis/water pair. Experimental data are fitted with the Ng et al., Yahia et al., BET, modified BET, and Do et al. models.

	Table 12. Average and 95%	confidence interval of HYBRID error fc	r n = 1000 bootstrap samples
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PVDC/water	Mean Error	95% CI of Error	Tripolis/Water	Mean Error	95% CI of Error
Ng et al.	0.08324	(0.0486, 0.1210)	Ng et al.	0.0127	(0.0043, 0.0247)
Yahia et al.	2.69468	(1.0143, 4.8338)	Yahia et al.	0.0903	(0.0341, 0.1678)
Mod. BET	0.51836	(0.2596, 0.8222)	BET	0.2576	(0.0550, 0.5013)
Mahle	0.92660	(0.1397, 1.8578)	Mod. BET	0.1471	(0.0613, 0.2460)
Sun and Chakraborty	1.12546	(0.2890, 2.1980)	Do et al.	0.4532	(0.0043, 0.0247)

Model	Mean Error	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Adsorption of water on	to PVDC							
Ng et al.	0.08324	-5.50	5.96	-1.77	78.50	1.50	12.96	-15.93
Yahia et al.	2.69468	31.27	44.37	36.24	143.27	39.27	52.37	19.36
Mod BET	0.51836	4.79	9.70	5.49	16.79	7.79	12.70	0.32
Mahle	0.92660	12.59	19.15	13.81	36.59	16.59	23.15	6.64
Sun and Chakraborty	1.12546	14.54	21.09	15.75	38.54	18.54	25.09	8.58
Adsorption of water on	to Tripolis							
Ng et al.	0.0127	-34.11	-22.64	-30.37	49.89	-27.11	-15.64	-44.53
Yahia et al.	0.0903	-8.62	4.48	-3.65	103.38	-0.62	12.48	-20.53
BET	0.2576	-8.03	-4.76	-7.69	-4.03	-6.03	-2.76	-11.01
Mod BET	0.1471	-12.76	-7.85	-12.05	-0.76	-9.76	-4.85	-17.23

Table 13. Optimal isotherm employing model selection criteria using HYBRID error mean of *n* = 1000 bootstrap samples.

5.6. Type-IV(b) Adsorption Isotherm

Depending on the pore width, the Type-IV isotherm is divided into two types, one with hysteresis and another without hysteresis, i.e., Type-IV(a) (pore width greater than 4 nm) and Type-IV(b) (pore width smaller than 4 nm), respectively [14]. Type-IV(b) is observed for the adsorbent having cylindrical and conical mesopores with a smaller width, which are entirely reversible and closed at the tapered end. Type-IV(b) adsorption isotherms are observed for the adsorption of argon at 87 K and nitrogen at 77 K onto IRMOF-74-V-hex having pore width less than 4 nm [36]. In this study, the Ng et al., modified Langmuir, Mahle, modified BET, and Tóth models are fitted with the experimental data of both pairs and presented in Figure 10.

The HYBRID error means and 95% CIs of errors are presented in Table 14 for adsorption of argon onto IRMOF-74-V-hex and nitrogen onto IRMOF-74-V-hex pairs. The Ng et al. model has a small amount of error, also confidence interval as compared to other models. This statement is also checked by determining various information criteria, as presented in Table 15. It is also observed that all methods except mAIC select the Ng et al. model as an optimal for argon adsorption, but nitrogen adsorption, and all ICs select the Ng et al. model. Since the majority of the ICs select the Ng et al. model, it signifies that information loss of the Ng et al. model is less when compared to other models for Type-IV(b) isotherm.



Figure 10. Type-IV(b) adsorption isotherms for (a) IRMOF-74-V-hex/argon pair and (b) IRMOF-74-V-hex/nitrogen pair. Experimental data are fitted with the Ng et al., modified BET, Mahle, modified Langmuir, and Tóth models.

IRMOF-74-V-hex/argon	Mean Error	95% CI of Error	IRMOF-74-V-hex/nitrogen	Mean Error	95% CI of Error
Ng et al.	0.95400	(0.8126, 0.9967)	Ng et al.	0.18451	(0.1124, 0.2435)
Mod. BET	2.71755	(1.9571,	Mod. BET	1.19510	(0.5642, 2.9856)
Mahle	4.24836	(3.2145 <i>,</i> 6.2541)	Mahle	1.18360	(0.4265, 3 2113)
Mod. Langmuir	2.68435	(1.2563, 4.1256)	Mod. Langmuir	0.53406	(0.0613, 2.1560)
Tóth	4.34000	(3.5671, 5.3461)	Tóth	1.65845	(0.4125, 2.6571)

Table 14. Average and 95% confidence interval of HYBRID error for *n* = 1000 bootstrap samples.

Table 15. Optimal isotherm employing model selection criteria using HYBRID error mean of *n* = 1000 bootstrap samples.

Model	Mean Error	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Adsorption of argo	on onto IRMOF	-74-A-hex						
Ng et al.	0.95400	-48.49	-37.03	-44.76	35.51	-41.49	-30.03	-58.92
Mod. BET	2.71755	-1.01	3.90	-0.31	10.99	1.99	6.90	-5.48
Mahle	4.24836	24.67	31.22	25.88	48.67	28.67	35.22	18.71
Mod. Langmuir	2.68435	6.34	17.80	10.07	90.34	13.34	24.80	-4.09
Tóth	4.34000	25.80	32.35	27.01	49.80	29.80	36.35	19.84
Adsorption of N2 of	onto IRMOF-74	-A-hex						
Ng et al.	0.18451	-135.57	-124.1	-131.84	-51.57	-128.5	-117.1	-145.9
Mod. BET	1.19510	-44.55	-39.64	-43.84	-32.55	-41.55	-36.64	-49.02
Mahle	1.18360	-19.79	-13.24	-18.58	4.21	-15.79	-9.24	-25.75
Mod. Langmuir	0.53406	-79.24	-67.78	-75.51	4.76	-72.24	-60.78	-89.66
Tóth	1.65845	-25.18	-18.63	-23.97	-1.18	-21.18	-14.63	-31.14

5.7. Type-V Adsorption Isotherm

Type-V is distinguished by its characteristic S-shaped isotherm, and it also demonstrates a hysteresis loop. Water adsorption onto different types of zeolites exhibits Type-V characteristics. In the present investigation, an AQSOA-Z01/water pair is considered for the analysis of the Type-V isotherm model. Kayal et al. [37] utilized D–A, modified Langmuir, and Sun and Chakraborty models for the adsorption of water onto AQSOA-Z01 at temperatures 25 °C, 40 °C, and 65 °C. The isotherms are fitted in the current study with Sun and Chakraborty, modified Langmuir, Mahle, D–A, and Ng et al. models presented in Figure 11.

The results of bootstrap mean HYBRID error, 95% CI, and IC values are presented in Table 16. The results show that the mean HYBRID error, 95% CI of errors, as well as values of all information criteria are small for Sun and Chakraborty model, as compared to all other models. This indicates that the Sun and Chakraborty model incurs the lowest information loss as compared to all other models taken into consideration.

The selection probabilities of two possible models, namely, the Sun and Chakraborty model and modified Langmuir model, are depicted in Figure 12. It is again evident from the figure that for the adsorption pair in concern, the selection probability of the Sun and Chakraborty model is much higher than that of the modified Langmuir model. The overall and pairwise proportion tests (as presented in Table 17) reveal that the Sun and Chakraborty model has significantly less information loss as compared to a modified Langmuir model.



Figure 11. Type-V adsorption isotherm of FAM-Z01/water pair; experimental data are fitted with the Sun and Chakraborty, modified Langmuir, Mahle, D–A, and Ng et al. models using the HYBRID error evaluation function.

Model	Mean Error	CI of HYBRID	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
D-A	0.5370	(0.3538, 0.7506)	-43.21	-38.46	-42.46	-31.21	-40.21	-35.46	-47.83
Mahle	0.9121	(0.4822, 1.4353)	-22.14	-15.81	-20.85	1.86	-18.14	-11.81	-28.30
modified Langmuir	0.2172	(0.1225, 0.3370)	-67.79	-56.71	-63.79	16.21	-60.79	-49.71	-78.58
GAB	2.6254	(1.9507, 3.3515)	13.92	18.67	14.67	25.92	16.92	21.67	9.30
Sun and Chakraborty	0.1453	(0.0741 <i>,</i> 0.2364)	-88.27	-81.94	-86.98	-64.27	-84.27	-77.94	-94.44

Table 16. Optimal isotherm employing model selection criteria using a HYBRID error mean of n = 1000 bootstrap samples.



Figure 12. Probability of selecting models for Type-V adsorption isotherms considering different information criteria using HYBRID errors.

Table 17. p-value of the overall	and pairwise test	of equality of the val	lues of minimum IC using
HYBRID error for $n = 1000$ bootst	rap samples.		

Test	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Ortomall	2.2 ×	2.2 ×	2.2 ×	2.2 × 10-	2.2 ×	2.2 ×	2.2 ×
Overall	10-16	10-16	10-16	16	10-16	10-16	10-16
Sun and Chakraborty vs.	2.0 ×	2.0 ×	2.0 ×	2.0 × 10-	2.0 ×	2.0 ×	2.0 ×
Mod. Langmuir	10-16	10-16	10-16	16	10-16	10-16	10-16

5.8. Type-VI Adsorption Isotherm

In Type-VI, the adsorption occurs in steps. Two isotherm data are considered in the current study; (i) methane adsorption onto MgO at 87.4 K investigated by Gay et al. [76] and (ii) methane onto graphite at 77.3 K examined by Bienfait et al. [77]. These isotherm data are fitted with the Yahia et al., Ng et al., D–A, modified Langmuir, and Mahle models, and the results are depicted in Figure 13.

To further investigate the models, mean HYBRID error and 95% confidence interval are determined, and the results are presented in Table 18. According to the results, the Yahia et al. model is the preferred model to describe the Type-VI isotherm, as it has the lowest mean error and 95% CI.

The information criteria are determined for all the models, and results are presented in Table 19. It is observed from the table that, except for mAIC, the values of all IC corresponding to Yahia et al. model are smaller than the other models, and this is true for both the adsorption pairs. Hence, it can be said that the information loss of the Yahia et al. model is less compared to other models.





Figure 13. Type-VI adsorption isotherms exhibited by (**a**) MgO/methane pair at 87.4 K and (**b**) graphite/methane pair at 77.3 K. Experimental data are fitted with the Yahia et al., Ng et al., D–A, modified Langmuir, and Mahle models using the HYBRID error evaluation function.

McO/mothers	Mean	95% CI of		Mean	95% CI of
MgO/methane	Error	Error	Graphile/Methane	Error	Error
Yahia et al.	0.1237	(0.0699,0.1835)	Yahia et al.	0.562948	(0.3545,0.7757)
Ng et al.	0.6007	(0.4107,0.7994)	Ng et al.	7.848831	(3.4595,13.359)
D-A	6.6061	(3.4087,10.022)	D-A	15.06557	(9.0459,22.345)
Mod. Langmuir	21.165	(12.654,30.267)	Mod. Langmuir	21.242790	(12.848,30.937)
Mahle	11.430	(6.3491, 17.249)	Mahle	12.461560	(7.7736,17.705)

Table 18. Mean HYBRID error and confidence interval of error for *n* = 1000 bootstrap samples.

Table 19. Optimal isotherm employing model selection criteria using HYBRID mean error considering n = 1000 bootstrap samples.

Model	Mean error	AIC	BIC	AICc	mAIC	AIC3	CAIC	ABIC
Adsorption of met	hane onto MgC)						
Yahia et al.	0.1237	-89.70	-69.73	-77.70	174.30	-77.70	-57.73	-107.27
Ng et al.	0.6007	-26.06	-4.43	-11.50	285.94	-13.06	8.57	-45.10
D-A	6.6061	47.45	52.44	48.13	59.45	50.45	55.44	43.05
Mod. Langmuir	21.1652	100.86	112.50	104.47	184.86	107.86	119.50	90.60
Mahle	11.4302	70.83	77.48	72.00	94.83	74.83	81.48	64.97
Adsorption of met	hane onto grap	hite						
Yahia et al.	56.29480	159.73	181.14	169.79	423.73	171.73	193.14	143.53
Ng et al.	784.88310	277.66	300.86	289.80	589.66	290.66	313.86	260.12
D-A	1506.55700	286.35	291.71	286.95	298.35	289.35	294.71	282.31
Mod. Langmuir	2124.27900	309.47	321.96	312.58	393.47	316.47	328.96	300.03
Mahle	1246.15600	280.00	287.14	281.03	304.00	284.00	291.14	274.61

6. Conclusions

In this study, relevant adsorption pairs for all of the IUPAC-classified adsorption isotherms are analyzed. The experimental isotherm data are fitted with 15 different isotherm models through generalized reduced gradient (GRG) non-linear optimization methods. Selected adsorption pairs have the same properties and curve patterns as their corresponding types. Here, one relevant adsorption pair data with more than one temperatures is considered for Type-I(b), Type-III, and Type-V; and two different relevant adsorption pairs with single temperature are considered for Type-I(a), Type-II, Type-IV(a), Type-IV(b), and Type-VI isotherms. The result of this study gives a clear insight into which model is suitable for a particular adsorption isotherm type. From the rigorous analysis of information criteria using bootstrap mean error, the present study confirms that the modified BET is suitable for Type-I(a) and Type-II; the Tóth model for Type-I(b); the GAB model for Type-III; the Ng et al. for Type-IV(a) and Type IV(b); the Sun and Chakraborty model for Type-V; and the Yahia et al. model for Type-VI, are the optimal models for the viewpoint of information losses. This study reveals that the 95% confidence intervals of the optimal isotherm models are smaller, and selection probabilities of the optimal isotherm models are more significant compared to the other isotherm models. The negligible p-value (close to zero) for overall and pairwise proportion test corresponding to each IUPAC-classified adsorption isotherm confirms that the models stated above as optimal are significantly favorable from the statistical standpoint, and the optimal model could also be applicable for other examples of a particular type. Therefore, the present study provides a universal approach for selecting the optimal model for any types of experimental data on adsorption isotherms. Researchers can use this approach to select the optimal isotherm model after plotting and matching their raw data with any of the eight types of IUPAC-classified isotherms. This will reduce the working hours as well as enhance the reliability of their analysis.

Abbreviations

ABIC	adjusted bayesian information criterion
ACF	activated carbon fiber
ACP	activated carbon powder
AHT	adsorption heat transformation
AIC	akaike information criterion
AICc	corrected akaike information criterion
BET	brunauer-emmet-teller
BIC	bayesian information criterion
BIDC	benzimidazole-derived carbons
CI	confidence interval
D-A	dubinin-astakhov
GAB	guggenheim-anderson-de boer
GRG	generalized reduced gradient
IC	information criterion
IRMOF	isoreticular metal-organic framework
IUPAC	international union of pure and applied chemistry
M-AC	mangrove based activated carbon
mAIC	modified akaike information criterion
MgO	magnesium oxide
PBA	polymer based adsorbent
РСВ	poorly crystalline boehmite

PVDC polyvinylidene chloride

- RMSD root-mean-square deviation
- RSS residual sum of squares
- WPT waste palm trunk

Author Contributions: Conceptualization, M.M.R. and B.B.S; Formal analysis, M.M.R. and M.M.; Investigation, M.M.R., B.B.S. and A.P.; Methodology, M.M.R. and A.Z.S.; Supervision, B.B.S.; Validation, M.M.R., A.P. and A.Z.S.; Writing—original draft, M.M.R. and M.M.; Correction and revision of manuscript, M.M.R., A.P., A.Z.S. and B.B.S.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Md. Amirul Islam and Shamal Chandra Karmaker from Kyushu University, Japan, for their help and suggestion.

Conflicts of Interest: The authors proclaim no conflict of interest.

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