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Reliable estimation of adsorption isotherm parameters using adequate pore size distribution

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Abstract−The equilibrium adsorption isotherm has a crucial effect on various characteristics of the solid adsorbent (e.g., pore volume, bulk density, surface area, pore geometry). A historical paradox exists in conventional estimation of adsorption isotherm parameters. Traditionally, the total amount of adsorb material (total adsorption isotherm) has been considered equivalent to the local adsorption isotherm. This assumption is only valid when the corresponding pore size or energy distribution (PSD or ED) of the porous adsorbent can be successfully represented with the Dirac delta function. In practice, the actual PSD (or ED) is far from such assumption, and the traditional method for prediction of local adsorption isotherm parameters leads to serious errors. Up to now, the powerful combination of inverse theory and linear regularization technique has drastically failed when used for extraction of PSD from real adsorption data. For this reason, all previous researches used synthetic data because they were not able to extract proper PSD from the measured total adsorption isotherm with unrealistic parameters of local adsorption isotherm. We propose a novel approach that can successfully provide the correct values of local adsorption isotherm parameters without any *a priori* and unrealistic assumptions. Two distinct methods are suggested and several illustrative (synthetic and real experimental) examples are presented to clearly demonstrate the effectiveness of the newly proposed methods on computing the correct values of local adsorption isotherm parameters. The so-called *Iterative* and *Optima* methods' impressive performances on extraction of correct PSD are validated using several experimental data sets.

Keywords: Adsorption Isotherm, Pore Size Distribution, Parameters Estimation, Iterative Method, Optima Method

INTRODUCTION

Adsorptive separation is achieved by either equilibrium or kinetic mechanisms. A majority of processes are equilibrium controlled because they operate through differences in equilibrium conditions. Kinetic separation is achieved by means of differences in diffusion rates of different molecules [1].

The equilibrium adsorption isotherm is essentially the most important characteristic of a solid adsorbent because it represents the adsorbent capacity, which is the primary key for nearly all practical applications. Many adsorbent characteristics (e.g., pore volume, bulk density, surface area, type of pores) have a crucial effect on the adsorption isotherm. On the other hand, the adsorption isotherm controls various characteristics of the adsorbents such as the pore size and energy distributions [2,3].

Both static and dynamic methods are well developed for gas (or liquid) - solid adsorption equilibrium and kinetic measurements. Gravimetric and volumetric methods are two important examples of the static method. Both methods are rather straightforward for single component isotherm measurement. Among the dynamic methods, column breakthrough method is one of the convenient methods for determining adsorption equilibrium and kinetic data [1].

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer-Emmett-Teller, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth, Koble-Corrigan, Sips, Khan, Hill, Flory-Huggins and Radke-Prausnitz isotherms among others), have been formulated in terms of three fundamental approaches [4]. Kinetic consideration is the first approach. Hereby, the adsorption equilibrium is defined as being a state of dynamic equilibrium, with both adsorption and desorption rates equal [5]. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models [6,7], and potential theory, as the third approach, usually conveys the main idea in the generation of a characteristic curve [8]. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [9].

All adsorption isotherm models are generally classified in monolayer isotherms and multilayer ones. Monolayer isotherms also include a vast variety of models which are presented by the number of involved parameters. To the point of above, the Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Flory-Huggins and Hill are the most practical two parameter isotherms. Three parameter ones are such as Redlich-Peterson, Sips, Toth, Koble-Corrigan. The most widely applied multilayer isotherm is Brunauer-Emmett-Teller, known as BET [10].

Up to now, the total amount of adsorb material (total adsorption isotherm) has been historically set equal to the local adsorption isotherm without specifying any *a priori* assumption. Afterwards,

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a proper nonlinear regression method is used to estimate the optimum local adsorption isotherm parameters. Two novel methods, *Iterative* and *Optima,* will be presented in this article and their successful performances will be validated using several synthetic and real experimental examples.

CONVENTIONAL METHOD FOR ESTIMATION OF ADSORPTION ISOTHERM PARAMETERS

As mentioned earlier, various empirical isotherms (5-6 groups) represent the relation between amounts of adsorbed material per unit mass of adsorbent versus the partial pressure of component under consideration in gas phase ($\theta(P_i)$). Assuming a proper model, for local adsorption isotherm ($\hat{\theta}$ (P_i, E)) the corresponding model parameters (kernel) can be estimated using the following integral equation:

$$\begin{aligned}\theta(P_i) &= \int_{\theta_{min}}^{\theta_{max}} \hat{\theta}(P_i,\ E)f(E)de \\ &= \int_{r_{min}}^{r_{max}} \hat{\theta}(P_i,\ r)f(r)dr \qquad (1)\end{aligned}$$

The above equations are known as the Fredholm integral of the first kind in mathematics. Up to now, the total amount of adsorb material (θ) has been historically set equal to the local adsorption isotherm ($\hat{\theta}$ (P_i, E)) without specifying any *a priori* assumption. This was the one and only way which always applied to find the optimum local adsorption isotherm (kernel) parameters accompanied by a proper nonlinear regression method. This assumption works only when f(E) is taken as the delta-Dirac function [11]. Otherwise, there is no guarantee that the amounts of θ and $\hat{\theta}$ would be equal or even similar. As the actual energy or pore size distribution deviates from delta-Dirac function, the difference between the total adsorption isotherm (θ) and the corresponding local adsorption isotherm ($\hat{\theta}$ (P_i, E)) becomes larger and larger.

1. Examples

To clearly illustrate this issue, the following synthetic examples are presented. In all three cases, the corresponding local adsorption isotherm ($\hat{\theta}$ (P_i, E)) is assumed to be Langmuir type with the following shape and parameters:

$$\hat{\theta}(P_i,\ E) = \frac{\theta_{max} k_0 e^{E/RT} P_i}{1 + k_0 e^{E/RT} P_i} \qquad \theta_{max} = 8.0 \frac{\text{mmole}}{\text{g}} \qquad k_0 = 0.2\ \text{kPa}^{-1} \quad (2)$$

Using the following relation between characteristic energy (E: Joule/mole) and pore size or half width of the slit shape mesopore (r: nm) of a meso-porous adsorbent [12]:

$$\frac{1}{E^2} = Mr^2 \qquad (3)$$

where M is a constant (6.944×10^{-9} $(J/mol)^{-2}nm^{-2}$). Substitution of E with r in Eq. (2) from Eq. (3) leads to:

$$\hat{\theta}(P_i,\ r) = \frac{\theta_{max} k_0 e^{1/\sqrt{MRTr}} P_i}{1 + k_0 e^{1/\sqrt{MRTr}} P_i} = \frac{\theta_{max} b P_i}{1 + b P_i} \qquad (4)$$

Replacing Eq. (4) in Eq. (1) and assuming delta-Dirac function over the center of corresponding distribution ($\hat{r} = 10$ nm) for PSD (f(r)) results to:

$$\hat{\theta}(P_i) = \int_{r_{min}}^{r_{max}} \theta(P_i,\ r)f(r)dr = \int_{r_{min}}^{r_{max}} \frac{\theta_{max} k_0 e^{1/\sqrt{MRTr}} P_i}{1 + k_0 e^{1/\sqrt{MRTr}} P_i} \delta(r - \hat{r})dr \qquad (5)$$

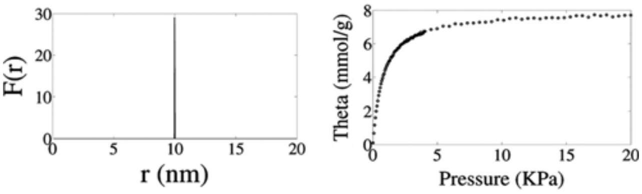

Fig. 1. Delta-Dirac function distribution assumed for PSD and the corresponding total adsorption isotherm computed via Eq. (2).

Fig. 1 illustrates the noisy total adsorption isotherm (assuming delta-Dirac function for PSD) which is contaminated with 1 percent noise drawn from uniform distribution (to mimic measurement error existing in the actual data).

As anticipated, nonlinear regression of Fig. 1 provides the values of isotherm parameters as θ_{max}=8.011 mmole/g and k_0=0.1990 kPa^{-1} which are almost equal to the original parameters assumed in Eq. (2). In the above regression, the corresponding known center of distribution ($\hat{r}$) should be used as a fixed parameter, otherwise, the value of k_0 may be far from the correct value, depending on the fitted value computed for $\hat{r}$. An iterative procedure will be presented later in section 3 to fix this problem.

In the second example, two other distributions with unit area are considered for PSD. The first one is a relatively flat Gaussian distribution (with $\hat{r}$=10 nm, σ=5 nm and w=0.1135) and the second distribution is a triple pick Gaussian. Fig. 2 shows both above distributions and the corresponding extracted total adsorption isotherms after integrating the following equations.

$$\theta(P_i) = \int_{r_{min}}^{r_{max}} \frac{\theta_{max} k_0 e^{1/\sqrt{MRTr}} P_i}{1 + k_0 e^{1/\sqrt{MRTr}} P_i} \left[w e^{\frac{(r-\hat{r})^2}{\sigma^2}} \right] dr \qquad (6)$$

$$\theta(P_i) = \int_{r_{min}}^{r_{max}} \frac{\theta_{max} k_0 e^{1/\sqrt{MRTr}} P_i}{1 + k_0 e^{1/\sqrt{MRTr}} P_i} \left[0.18 e^{\frac{(r-5)^2}{2.0^2}} \right.$$

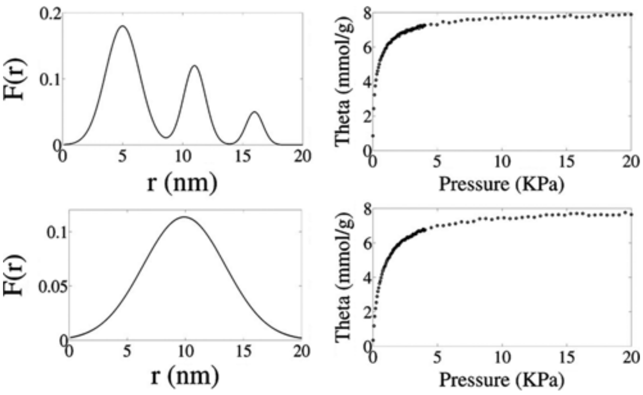

Fig. 2. Single and triple pick distributions each with unit area assumed for PSD and the corresponding total adsorption isotherms.

$$+0.12e^{\frac{(r-11)^2}{1.3^2}}+0.05e^{\frac{(r-16)^2}{1.0^2}}\Bigg]dr \tag{7}$$

Once again, the extracted total adsorption isotherms are contaminated with 1 percent noise drawn from uniform distribution. The nonlinear regression of total adsorption isotherms shown in Fig. 2 provides the following values for isotherm parameters:

a) Gaussian: θ_{max}=7.847 and k_0=0.250.

b) Triple pick distribution: θ_{max}=7.760 and k_0=0.320.

As can be seen, the values of θ_{max} are comparable with the original value of 8.0, but k_0 is far from the originally assumed value even when the correct value of the center of distribution ($\hat{r}$) is assumed to be known. The following equation is used to determine the effective center of distribution for triple pick case.

$$r_e=\Sigma_{i=1}^{3}(r_iA_i)/A_t=7.64 \text{ nm} \tag{8}$$

As the final case study, the previous example is repeated while the unit area assumption of PSD is relaxed for both single and triple pick distributions. The following equations are used to compute the corresponding total adsorption isotherms and the results are contaminated with 1 percent uniform noise as plotted in Fig. 3.

$$\theta(P_i)=\int_{r_{min}}^{r_{max}}\frac{\theta_{max}k_0e^{1/\sqrt{M}RTr}P_i}{1+k_0e^{1/\sqrt{M}RTr}P_i}\Bigg[0.227e^{\frac{(r-10)^2}{5^2}}\Bigg]dr \tag{9}$$

$$\theta(P_i)=\int_{r_{min}}^{r_{max}}\frac{\theta_{max}k_0e^{1/\sqrt{M}RTr}P_i}{1+k_0e^{1/\sqrt{M}RTr}P_i}\Bigg[0.40e^{\frac{(r-6)^2}{2.0^2}}$$

$$+0.18e^{\frac{(r-11)^2}{1.3^2}}+0.10e^{\frac{(r-15)^2}{1.0^2}}\Bigg]dr \tag{10}$$

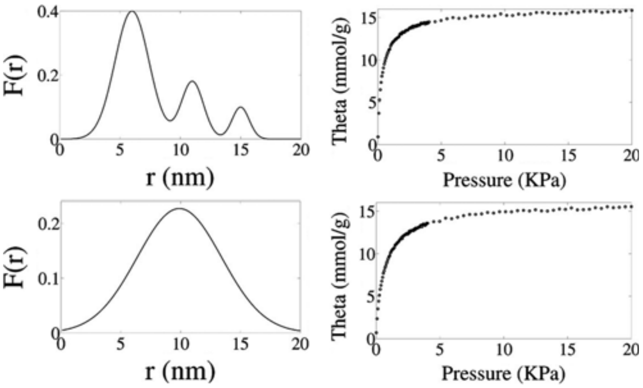

Fig. 3. Single and triple pick distributions with non-unity areas assumed for PSD and the corresponding total adsorption isotherms.

As before, nonlinear regression of noisy isotherms provides the following values for isotherm parameters when the correct value of is assumed to be known:

a) Gaussian: θ_{max}=15.730 and k_0=0.250.

b) Triple pick distribution: θ_{max}=15.840 and k_0=0.280,

which are both relatively far from the originally assumed values. The effective center of distribution for triple peak case computed via Eq. (8) is equal to 7.85.

Table 1 reviews the above-computed results for total adsorption isotherm parameters, calculated via non-linear regressions for all three examples. Evidently, the traditional method for estimation of local adsorption isotherm parameters fails when the pore size distribution deviates from the delta Dirac function even when the correct value for the center of distribution ($\hat{r}$) is assumed as a fixed parameter. Table 2 shows the non-linearly regressed values of the fitted parameters when no *a priori* assumption is made for $\hat{r}$. Evidently, most of the predicted values are totally wrong and very far from the correct values.

In the preceding sections, two following methods have been presented for proper estimation of local adsorption isotherm parameters.

- ✓ The first method uses an iterative procedure combined with linear regularization theory to achieve this goal.
- ✓ In the second approach, the actual PSD is initially determined from experimental data (e.g. Hg porosimetry) or a suitable

Table 1. Review of fitted parameters for 3 synthetic examples with different PSD's (Center of distribution ($\hat{r}$) is assumed initially)

Parameter	Original values	A=1			A=2	
		delta-Dirac function ($\hat{r}$=10)	Flat gaussian ($\hat{r}$=10)	Triple peak ($\hat{r}_e$=7.64)	Flat gaussian ($\hat{r}$=10)	Triple peak ($\hat{r}_e$=7.85)
θ_{max} (mmole/g)	8.0	8.011	7.8470	7.7600	15.7300	15.7300
k_0 (kPa^{-1})	0.2	0.1990	0.2500	0.3200	0.2500	0.2800
b (kPa^{-1})	1.3035	1.2970	1.6295	2.0857	1.6295	1.8250

Table 2. Review of fitted parameters for synthetic examples with different PSD's (no *a priori* assumption is made for $\hat{r}$)

Parameter	A=1			A=2	
	delta-Dirac function	Flat gaussian	Triple peak	Flat gaussian	Triple peak
θ_{max} (mmole/g)	8.011	7.847	7.760	15.730	15.840
k_0 (kPa^{-1})	0.132	0.094	1.042	0.044	1.010
$\hat{r}$ (nm)	8.190	6.620	14.930	5.200	17.440
b (kPa^{-1})	1.3019	1.5955	3.6572	1.6182	2.9588

PSD is first computed via the independent methods of SHN1 or SHN2 [2,3]. Afterwards, a multidimensional optimization technique is employed to directly compute the optimal values of local adsorption isotherm parameters (such as: θ_{max} and k_0) for previously specified distribution.

ITERATIVE METHOD FOR ESTIMATION OF CORRECT LOCAL ADSORPTION ISOTHERM PARAMETERS

The following steps are used to compute the correct values of local adsorption isotherm parameters in an iterative method as shown in Fig. 4.

1) Adequate non-linear regression method should be used to find the initial sub-optimal values for local adsorption isotherm parameters ($\hat{r}$, θ_{max} and k_0).

2) The values of (θ_{max} and k_0) found above should be used to compute approximate PSD via inverse theory coupled with linear regularization technique. This issue is briefly explained in section 3.1.

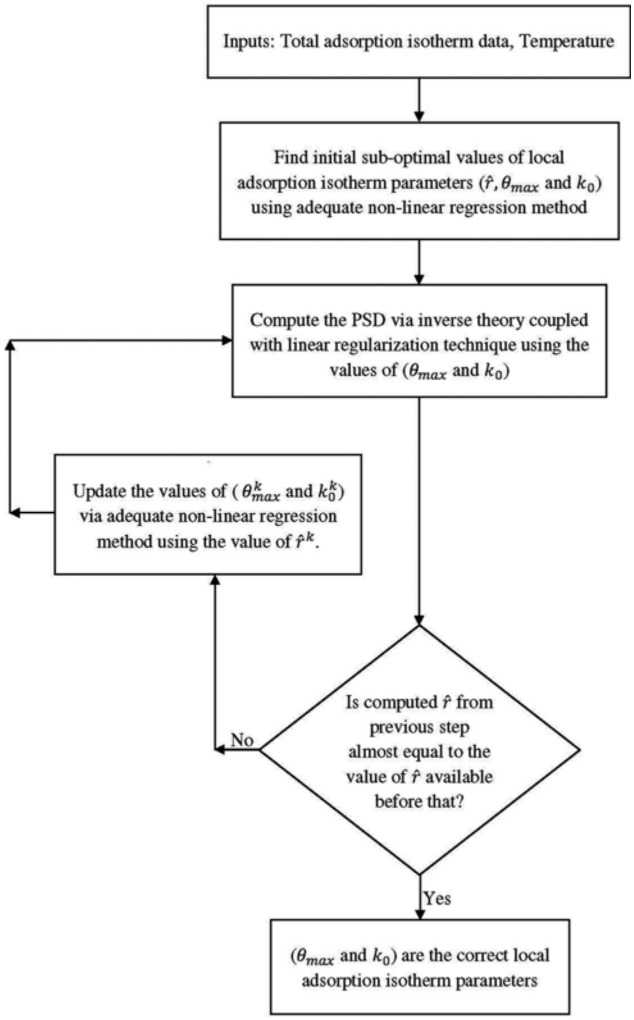

Fig. 4. Flow chart of the newly proposed method for estimation of correct local adsorption isotherm parameters.

3) The termination criteria should be checked to ensure $\hat{r}$ value extracted from PSD found in the previous step is converged.

4) The values of (θ^k_{max} and k^k_0) should be updated via appropriate non-linear regression for known value of $\hat{r}^k$ computed in step 2.

5) Return to step 2

1. A Brief Overview of Inverse Theory and Linear Regularization Technique

Eq. (1) can be viewed as the problem of finding an unknown function u(x) from a given set of noisy exemplars (x_i, y_i, i=1, 2, …, N) via the following equation:

$$y_i = \int r_i(x)u(x)dx + \varepsilon_i \tag{11}$$

The relationship between u(x) and each measured outputs y_i's, is defined by its own linear response kernel $r_i(x)$ and ε_i is the measurement error associated with the i^th^ experiment. The kernel $r_i(x)$ may represent a narrow instrumental response in which case y_i is an approximation to u(x). Alternatively, the measured responses (y_i's) might "live" in an entirely different function space from u(x).

Given the y_i's, the kernels $r_i(x)$'s and perhaps some information about the measurement errors ε_i's (e.g., their covariance matrix $\Sigma_{ij} \equiv \mathrm{Cov}[\varepsilon_i, \varepsilon_j]$), the problem is to devise a procedure to find a good statistical estimator of u(x) which will be denoted as $\underline{\hat{u}}(x)$. This is an inherently ill-posed issue known as an inverse problem. Depending on the smoothness of the kernel $r_i(x)$, sharp variations in the underlying function u(x) are smoothed (damped) out by the integration. Conversely, small variations in the data, y_i's, may lead to large variations in u(x). The problem is further compounded by the presence of noise in the data [2,11].

In practice, we are not interested in every point of the continuous function u(x) and a large number M of evenly spaced discrete points x_j, j=1, 2, …, M will suffice. Evidently, M must be large enough so that neither $\hat{u}(x)$ nor $r_i(x)$ varies significantly between two successive x_j's. For a sufficiently dense set of x_j's, we should use minimum norm concept ($\|R\underline{\hat{u}} - \underline{y}\|^2$) to replace the integral with the following set of linear equations using trapezoidal rule [11]:

$$(R^T R)\underline{\hat{u}} = R^T \underline{y} \tag{12}$$

where $\underline{y}$ and $\underline{\hat{u}}$ are vectors of size N and M, respectively, and the elements of the N×M matrix R are defined by $R_{ij} = r_i(x_j)(x_{j+1} - x_j)$, i=1, …, N & j=1, …, M.

The direct solution of Eq. (12) is hopeless and should be avoided. Since M is much greater than N, the M×M matrix $R^T R$ will be singular and the equation will have a large number of highly degenerate solutions. We may use singular value decomposition (SVD) technique to select the optimum solution with minimum norm from the infinite possible solutions. It is evident, however, that the SVD will find a large number of zero singular values, which results in losing most of the information content of matrix R.

In a more effective approach, the ill-posed inverse problem can be stabilized by imposing some *a priori* information about the unknown underlying function u(x) as a constraint on the original least square merit function. Based on our *a priori* information about the final solution (PSD), the previous set of linear equations converts to the following equation:

$$(R^T R + \lambda \Omega)\underline{\hat{u}} = R^T \underline{y} \tag{13}$$

Table 3. *Iterative* method results for synthetic examples (I: delta-Dirac function, II: Flat Gaussian, III: Triple peak)

Iter.	θ_{max} (mmole/g)					k_0 (kPa^{-1})					$\hat{r}$ (nm)				
	A=1			A=2		A=1			A=2		A=1			A=2	
	I	II	III	II	III	I	II	III	II	III	I	II	III	II	III
1	8.01	7.85	7.76	15.73	15.84	0.132	0.094	1.042	0.044	1.010	8.19	6.62	14.93	5.20	17.47
2	8.01	7.85	7.76	15.73	15.84	0.162	0.116	0.940	0.061	0.901	8.50	7.14	13.78	5.72	15.79
3	8.01	7.85	7.76	15.73	15.84	0.180	0.133	0.790	0.092	0.800	9.38	7.54	12.21	6.53	14.34
4	8.01	7.85	7.76	15.73	15.84	0.192	0.160	0.621	0.125	0.721	9.82	8.14	10.55	7.33	13.27
5	8.01	7.85	7.76	15.73	15.84	**0.200**	0.197	0.520	0.143	0.632	10.02	8.95	9.58	7.74	12.13
6	8.01	7.85	7.76	15.73	15.84	**0.200**	**0.203**	0.430	0.161	0.493	10.02	9.20	8.72	8.15	10.45
7		7.85	7.76	15.73	15.84		**0.203**	0.361	0.170	0.398		9.20	8.07	8.34	9.33
8			7.76	15.73	15.84			0.316	0.180	0.339			7.63	8.57	8.64
9			7.76	15.73	15.84			0.249	0.188	0.305			7.11	8.74	8.23
10			7.76	15.73	15.84			**0.208**	0.198	0.282			6.94	8.94	7.95
11			7.76	15.73	15.84			**0.208**	**0.205**	0.254			6.94	9.15	7.61
12				15.73	15.84				**0.205**	0.229				9.15	7.30
13					15.84					0.212					7.09
14					15.84					**0.188**					6.77
15					15.84					**0.188**					6.77

where λ is called as the level of regularization. Assuming λ and Ω are chosen so that ($R^TR+\lambda\Omega$) is non-singular, the above system admits a unique solution $\underline{\hat{u}}_\lambda$. Evidently, increasing λ pulls the solution $\underline{\hat{u}}_\lambda$ away from fitting the experimental data (information content of matrix R) towards our *a priori* information.

The form of matrix Ω strongly depends on the nature of the *a priori* information. For example, if the solution is practically zero in the entire input domain except for a relatively narrow region (as in the case of PSD), then the zero order regularization technique provides the optimum distribution by replacing Ω with unit matrix I_M. Similarly, if the unknown $\underline{\hat{u}}_\lambda$ is approximately a constant, then the first order regularization technique leads to:

$$(R^TR+\lambda B^TB)\underline{\hat{u}}=R^T\underline{y} \tag{14}$$

where, B is the (M−1)×M matrix given by,

$$B=\begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 \\ . & . & . & . & . \\ . & . & . & . & . \\ 0 & 0 & 0 & -1 & 0 \end{bmatrix} \tag{15}$$

Note that the (M–1)×M matrix B has one fewer row than column. Consequently, the M×M matrix $\Omega=B^TB$ is degenerate and has at least one zero eigenvalue (for the unknown constant). We may anticipate that the experimental data contains sufficient information to pick up the appropriate value of the constant [11]. Using similar approach, matrix Ω can be easily found for higher orders of regularization.

After constructing matrix R and selecting proper order of regularization technique (with appropriate form of matrix B), the optimal level of regularization parameter (λ^*) should be selected to establish the best stabilization of the solution vector $\underline{\hat{u}}_\lambda$. A concise review of various criteria (e.g., leave one out cross validation (LOOCV), L-curve (LC), U-curve (UC) and modified L-curve (MLC)) for automatic selection of optimum regularization parameter (λ^*) is presented in our previous article [3].

2. Predictions of *Iterative* Method for Previous Synthetic Examples

The novel *iterative* calculation procedure outlined in Fig. 4 is employed to compute the correct local adsorption isotherm parameters of various examples presented earlier in section 2.1. All intermediate results and final values are shown in Table 3. Evidently, our newly proposed method can successfully estimate the true local adsorption isotherm parameters even in the presence of relatively large noises. Moreover, as the original distribution approaches delta Dirac function distribution, the number of iterations is reduced appreciably.

Fig. 5 shows the plot of intermediate results for k_0 values presented in Table 3. Interestingly, for triple peak distributions, the intermediate results decrease during the iterations while the reverse phenomenon is observed for single peak distributions. In other words, the initial values for k_0 are irrelevant and the presented method converges almost for all initial values whether it is higher or lower

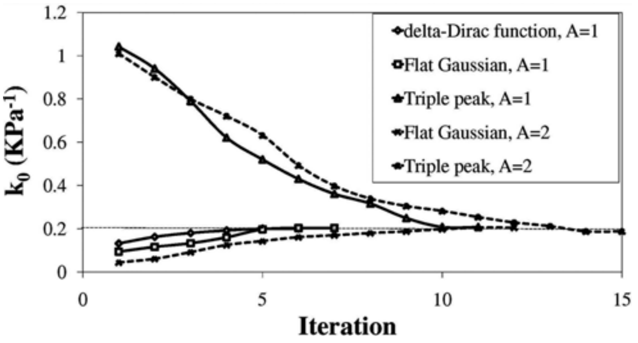

Fig. 5. Calculation results for k_0 using our newly proposed method and convergence of all examples to the true value.

from the actual value.

3. Application of *Iterative* Method for Real Case Studies

The synthetic examples used in the previous section demonstrated the impressive capabilities of the newly proposed method for prediction of the true local adsorption isotherm parameters from different sets of noisy total isotherms. In this section, three real case studies (i.e., experimental total isotherms borrowed from literature [13]) are used along with the corresponding measured (actual) pore size distributions to demonstrate the reliable performance of our iterative algorithm. The following comparative study focuses on comparison of the newly proposed method with the conventional procedure for evaluation of local adsorption isotherm parameters from experimental nitrogen physical adsorption isotherms (at 77 K) measured on a series of controlled-pore glasses (CPG) with wide range of nominal pore sizes.

Fig. 6 depicts three total isotherms for different CPG adsorbents and the corresponding actual pore size distributions measured via mercury porosimetry and borrowed from Solcova et al [13]. Table 4 presents all intermediate results and final values using the *iterative* method with no unrealistic assumptions. The results shown in bold and italics (first iteration) correspond to the conventional method, which are invalid especially for k_0 and $\hat{r}$ values.

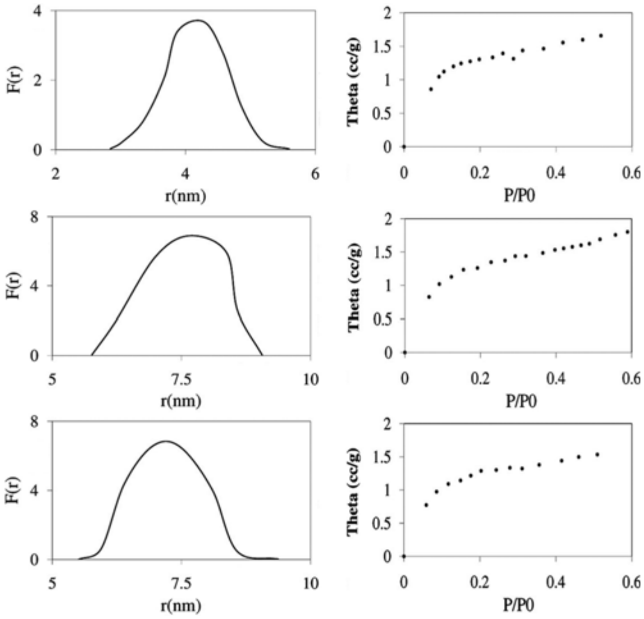

Fig. 6. Nitrogen physical adsorption isotherms (at 77 K) and corresponding actual PSD measured via mercury porosimetry. Top: CPG80, middle: CPG120, Bottom: CPG159.

Table 4. Calculation results for 3 real case studies via Iterative method (I: CPG80, II: CPG120, III: CPG159)

Iter.	θ_{max} (mmole/g)			k_0 (kPa^{-1})			$\hat{r}$ (nm)		
	I	II	III	I	II	III	I	II	III
1	***1.81***	***1.94***	***1.68***	***1.934***	***0.035***	***0.037***	***9.50***	***3.27***	***3.13***
2	1.81	1.94	1.68	1.336	0.013	0.051	8.16	2.81	3.30
3	1.81	1.94	1.68	0.830	0.234	0.231	6.65	4.92	4.52
4	1.81	1.94	1.68	0.357	0.271	0.556	5.13	5.12	5.53
5	1.81	1.94	1.68	0.308	0.465	0.621	4.92	5.36	5.83
6	1.81	1.94	1.68	0.181	0.727	**0.774**	4.32	6.44	6.34
7	1.81	1.94	1.68	**0.130**	**0.756**	**0.774**	3.92	6.74	6.34
8	1.81	1.94		**0.130**	**0.756**		3.92	6.74	

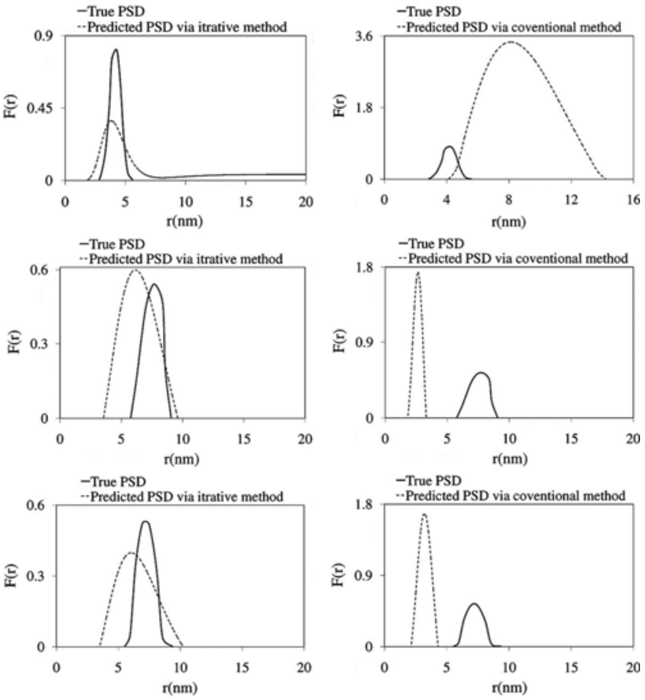

Fig. 7. Comparisons of predicted PSD with the true distributions. Top: CPG80, Middle: CPG120, Bottom: CPG159.

Fig. 7 compares the predicted normalized PSD's via our newly proposed *iterative* algorithm and conventional method with original measured mercury porosimetry data. As it can be seen, the *Iterative* method successfully predicts the position of the peak locations, heights and spreads of all distributions, while the conventional method fails in one, two (CPG-120, CPG-159) or three (CPG-80) of the above parameters.

The unrealistic values of isotherm parameters found via the traditional method are the key reason for why never any inverse theory and linear regularization based method is employed real case studies or experimental data to extract the PSD by using those parameters. Even for correct local adsorption isotherms (kernel), erroneous isotherm parameters will lead to incorrect PSD's, as it can be easily anticipated. This is why all studies up to now use synthetic adsorption isotherms for extraction of PSDs [14-17].

The above method simultaneously and successfully finds true local adsorption isotherm parameters and the corresponding center of distribution ($\hat{r}$). The value of $\hat{r}$ for single peak has physical meaning, but for multiple peak distributions the predicted value has no real physical meaning. It may be considered as a weighted average of multiple peak locations. The following advanced methods directly and independently find the PSD from experimental condensation or adsorption (when accompanied with condensation) data. Using this PSD, one can find the correct local adsorption isotherm parameters by resorting to nonlinear optimization (via gradient descent), as will be discussed later in this article.

Since the new advanced techniques of SHN1 and SHN2 only perform adequately when condensation or adsorption (accompanied with condensation) are involved, therefore the above Langmuir type isotherm examples cannot be used and other local adsorption isotherms (such as BET) should be considered. This issue will receive proper attention in section 5.

ADVANCED NUMERICAL TECHNIQUES FOR *A PRIORI* ESTIMATION OF PSD

Extraction of energy or pore size distribution from Eq. (1) is an ill posed problem [11]. For a given local adsorption isotherm one may find infinite optimal distributions which satisfy Eq. (13) for various values of regularization parameters. Obviously, only one of these numerous distributions belongs to the actual ED or true PSD of the real adsorbent under consideration.

The optimally unique extracted distribution for PSD or AED completely depends on the choice of local adsorption isotherm (kernel) and the level of regularization. Various kernels can be used for a given adsorption isotherm, and each kernel may lead to an entirely different solution for PSD or ED. Evidently, recruitment of a method which does not require any kernel would be very desirable and advantageous.

Two novel methods of SHN1 and SHN2 were recently presented for reliable prediction of the pore size distributions of heterogeneous solid adsorbents based on inverse theory using mere condensation data or condensation phenomenon accompanied with a prior adsorbed layer. Detailed description of these methods has received sufficient attention in corresponding published articles [2,3]. A brief overview will be presented to familiarize the reader with the essence of the proposed methods.

The following integrals are usually used to find the PSD of a heterogeneous solid adsorbent (f(r)) from a set of noisy measured data available for the amount of adsorbed material at a given sets of pressures (P_i; i=1, …, n):

$$\Psi(P_i)=\int_0^{r_K(P_i)} f(r)dr \qquad \text{(mere condensation)} \tag{16}$$

$$\Psi(P_i)=\int_0^{r_K(P_i)} f(r)dr+t\int_{r_K(P_i)}^{r_{max}} \frac{2f(r)}{r}dr$$

$$\text{(condensation with } a\ priori \text{ adsorbed layer)} \tag{17}$$

The above ill-posed problems of finding f(r) from above integrals can be replaced with a set of linear algebraic equations $\{(R^TR+\lambda B^TB)\underline{f}(r)=R^T\underline{\Psi}\}$, using a combination of inverse theory and linear regularization technique. In this equation, the $N\times M_t$ coefficient matrix $R\in\Re^{[N\times\Sigma_{i=1}^{N}M(P_i)]}$[1] has usually many more columns than its rows (depending on the order of regularization technique used), the overall PSD column vector ($\underline{f}\in\Re^{[\Sigma_{i=1}^{N}M(P_i)\times 1]}$) has dimensions of $[\Sigma^N_{i=1}M(P_i)\times 1]$, $\underline{\Psi}$ is $N\times 1$ a vector and λ is the regularization parameter. Detailed descriptions of various R matrices corresponding to Eqs. (16) and (17) have been presented elsewhere [2,3].

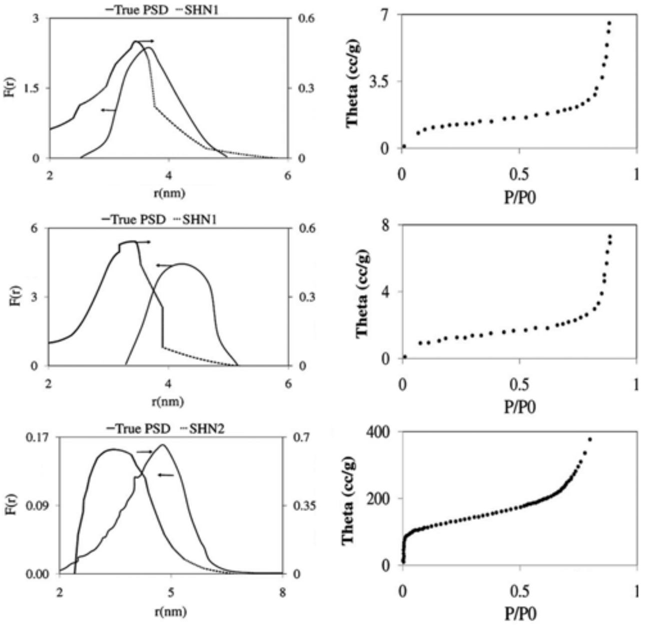

Fig. 8. Nitrogen physical adsorption isotherms (at 77 K) and corresponding actual PSD measured via mercury porosimetry and extracted with SHN1 and SHN2 methods. Top: CPG69, Middle: CPG75, Bottom: CMC3.

Evidently, dimensions of the matrix B depend on the order of regularization technique employed to stabilize the final PSD solution (f(r)). Using zero order regularization technique, matrix B simply reduces to the identity matrix of $I\in\Re^{[\Sigma_{i=1}^{N}M(P_i)\times\Sigma_{i=1}^{N}M(P_i)]}$.

1. PSD Extraction for Real Case Study Via SHN1 and SHN2

Fig. 8 illustrates three real total isotherms for various CPG adsorbents and the corresponding actual pore size distributions measured via mercury porosimetry (borrowed from Solcova et al. [13]) and computed PSD's extracted with SHN1 and SHN2 methods. As can be seen, both methods successfully recover the correct PSD's from real adsorption isotherms.

OPTIMAL SELECTION OF LOCAL ADSORPTION ISOTHERM PARAMETERS USING KNOWN PSD

The present method (which will be referred to as *Optima* from now on) uses an *a priori* specified PSD (either measured experimentally via mercury porosimetry or computed theatrically). In the absence of measured PSD's, SHN1 and SHN2 methods can successfully predict PSD's from real adsorption isotherms. Furthermore, a proper local adsorption isotherm should be selected. Then, the following nonlinear optimization method provides the optimal local adsorption isotherm parameters.

The more robust gradient descent optimization technique is used in this work to find the minimum of the ordinary least square (OLS) cost function as described below:

$$\mathfrak{C}=\frac{1}{2}\Sigma_{i=1}^{n}(\varphi_i-\varphi(P_i))^2 \tag{18}$$

In the above equation, φ_i's are the real adsorbed amounts measured via n experiments (i=1, 2, …, n) and $\varphi(P_i)$ values are the predicted

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[1] $M(P_i)$ is the number of discretized intervals between r_K (P_i-1) and $r_K(P_i)$ and N is the number of data points of any isotherm.

(estimated) adsorbed amounts computed from the following relation using proper local adsorption isotherm (such as BET) in term of pore size (r):

$$\varphi(\mathrm{P}_i)=\frac{\theta(\mathrm{P}_i)}{\theta_{max}}=\int_{r_{min}}^{r_{max}}\frac{\hat{\theta}(\mathrm{P}_i,\mathrm{r})}{\theta_{max}}\mathrm{f(r)dr}\qquad \mathrm{i=1,2,\ldots,n}$$

$$=\int_{r_{min}}^{r_{max}}\frac{(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)(\mathrm{P/P}_0)_i}{(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i)}\mathrm{f(r)dr}\quad (19)$$

The original BET local adsorption isotherm is often presented in the following form [18]:

$$\hat{\theta}(\mathrm{P}_i,\mathrm{E})=\frac{\theta_{max}\cdot\mathrm{C}\cdot(\mathrm{P/P}_0)_i}{(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+\mathrm{C}\cdot(\mathrm{P/P}_0)_i)}\quad (20)$$

Substituting Eqs. (3) and $\mathrm{C}=(\mathrm{k}_0\mathrm{e}^{E/RT-1})^2$ in Eq. (20) leads to:

$$\hat{\theta}(\mathrm{P}_i,\mathrm{r})=\frac{\theta_{max}(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i}{(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i)}\quad (21)$$

The integral equation of (19) can be approximated with the following summation of m intervals:

$$\varphi(\mathrm{P}_i)=\Sigma_{j=1}^{m}\frac{(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i}{(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i)}\mathrm{f(r)}_j\Delta\mathrm{r}_j,$$

$$\begin{cases}\mathrm{i=1,2,\ldots,n}\\ \mathrm{j=1,2,\ldots,m}\end{cases}\quad (22)$$

To ensure the accuracy, m (number of internal segments) is usually selected much greater than n (number of measured data points). To minimize OLS cost function of Eq. (18), the following differentiation (with respect to k_0) should be performed.

$$\frac{\mathrm{d}\mathfrak{C}}{\mathrm{dk}_0}=\Sigma_{i=1}^{n}\left[(\varphi_i-\varphi(\mathrm{P}_i))\cdot\frac{\mathrm{d}(\varphi(\mathrm{P}_i))}{\mathrm{dk}_0}\right]\quad (23)$$

$$\frac{\mathrm{d}(\varphi(\mathrm{P}_i))}{\mathrm{dk}_0}$$

$$=\frac{[(\mathrm{P/P}_0)_i-2(\mathrm{P/P}_0)_i^2+(\mathrm{P/P}_0)_i^3]\cdot[2\mathrm{e}^{1/\sqrt{M}RTr}(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)]}{[(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+\mathrm{C}\cdot(\mathrm{P/P}_0)_i)]^2}\quad (24)$$

The optimum value of parameter k_0 can be computed using any classic optimization technique. Gradient descent technique (with fixed step length (η)) is used here to update k_0 values.

$$\mathrm{k}_0^{k+1}=\mathrm{k}_0^{k}-\eta\frac{\mathrm{d}\mathfrak{C}}{\mathrm{dk}_0}\quad (25)$$

The method converges when the termination criteria of $\mathfrak{C}'=\mathrm{d}\mathfrak{C}/\mathrm{dk}_0$ is less than any properly defined tolerance.

The above optimization algorithm (*optima* method) simultaneously uses the total adsorption isotherm (φ_i, i=1, 2, …, n) and corresponding PSD's (measured ones or computed via SHN1 and SHN2) to successfully estimate the optimal local adsorption parameters as shown in the following synthetic and real examples.

1. Synthetic and Real Examples for *Optima* Method

To clearly illustrate the impressive performance of the *Optima* method, the following examples are presented. Conventional and the iterative methods are used initially for both synthetic and real case studies to predict proper local adsorption isotherm parameters. Afterwards, the same optimal parameters are computed via the *Optima* method.

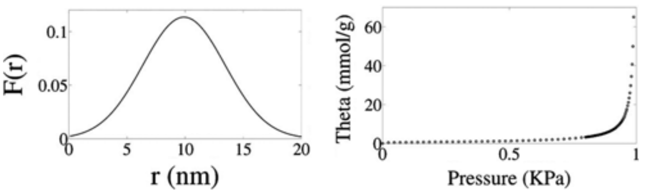

Fig. 9. Single pick distributions with unit area assumed for PSD and the corresponding total adsorption isotherms.

1-1. Synthetic Examples

As mentioned earlier, the BET local adsorption isotherm ($\hat{\theta}$ (P_i, E)) works better than Langmuir for condensation associated cases of SHN1 and SHN2 methods. The original parameters used to generate synthetic data are assumed to be (θ_{max}=0.65 mmole/g, k_0= 1.45 kPa^{-1}). As before, Gaussian distribution (with $\hat{\mathrm{r}}$=10 nm, σ=5 nm and w=0.1135) is used for PSD of synthetic data generated via the following equation:

$$\theta(\mathrm{P}_i)=\int_{r_{min}}^{r_{max}}\frac{(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i}{(1-(\mathrm{P/P}_0)_i)(1-(\mathrm{P/P}_0)_i+(\mathrm{k}_0\mathrm{e}^{1/\sqrt{M}RTr}-1)^2(\mathrm{P/P}_0)_i)}\left[\mathrm{we}^{\frac{(r-\hat{r})^2}{\sigma^2}}\right]\mathrm{dr}\quad (26)$$

Fig. 9 depicts the noisy total adsorption isotherm which is contaminated with 1 percent noise drawn from uniform distribution and the corresponding assumed PSD.

Table 5 compares the final values obtained from various methods. As can be seen, the conventional method predicted invalid values especially for k_0 and $\hat{\mathrm{r}}$. But obviously, final results estimated via *Iterative* and *Optima* methods are almost the same of the originally assumed values. Note that *Optima* method is much faster but limited to the cases where condensation is involved.

1-2. Real Case Studies

The synthetic example presented in the previous section revealed the impressive performances of two *Iterative* and *Optima* methods for prediction of the true local adsorption isotherm parameters from a set of synthetic noisy data where the total adsorption isotherm was generated via BET local adsorption isotherm. In this section, two real case studies will be presented to compare the performance of both *Iterative* and *Optima* methods in capturing the true pore size distributions using BET local adsorption isotherm.

Table 5. Comparison of *Optima* and Iterative methods with conventional method for synthetic data

Method	θ_{max} (mmole/g)	k_0 (kPa^{-1})	$\hat{\mathrm{r}}$ (nm)
Original values	0.650	1.450	10.00
Conventional	0.645	2.596	15.75
Iterative	0.645	1.450	10.58
Optima	0.650	1.378	10.00

Table 6. Comparison of *Optima* and *Iterative* methods with conventional method for real data

Method	θ_{max} (mmole/g)		k_0 (kPa^{-1})		$\hat{r}$ (nm)	
	CPG69	CPG75	CPG69	CPG75	CPG69	CPG75
Conventional	0.650	0.704	1.433	2.030	7.81	10.11
Iterative	0.650	0.704	0.076	0.136	3.51	4.07
Optima using Hg. porosimetry PSD	0.650	0.704	0.171	0.198	3.64	4.29
Optima using SHN1 computed PSD	0.650	0.704	0.162	0.073	3.44	3.41

For real case studies, the correct PSD's are initially extracted via SHN1 method as shown in Fig. 8. Evidently, the third data set of Fig. 8 cannot be used in this section, since its total adsorption isotherm is far from BET local adsorption isotherm.

Table 6 compares the final values obtained for BET local adsorption isotherm parameters via *Optima* and Iterative methods with the values found from conventional method. As mentioned earlier, the values of the conventional method are the initial values obtained in *iterative* method at first iteration. Evidently, both Iterative and *Optima* methods were able to successfully estimate the true local adsorption isotherm parameters especially the center of distribution ($\hat{r}$) for two adsorbents. Conventional method results are entirely unrealistic as they were supposed to be.

CONCLUSIONS

Two new methods for estimating the isotherm parameters for local absorption were presented. The first method (*Iterative*) is based on the recurrence algorithm, while the second method (*Optima*) minimizes a cost function to predict the local adsorption isotherm parameters. Both methods are able to correctly estimate the local adsorption isotherm parameters using powerful inverse theory coupled with linear regularization technique.

The *Optima* method should be equipped with a pre-specified *a priori* PSD (measured by experimental methods or calculated via SHN1 and SHN2). Furthermore, it employs an appropriate multidimensional optimization technique to directly predict the optimized local adsorption isotherms parameters.

Promising performances of both proposed methods were clearly demonstrated by resorting to several illustrative synthetic and real experimental examples. It was shown that both *Iterative* and *Optima* methods can provide accurate and reliable values for the local adsorption isotherm parameters, when the selected local adsorption isotherm is compatible with the total adsorption isotherm. The *Optima* method converges much faster but it is relatively more complex than the *Iterative* method.

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