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Robust PSD determination of micro and meso-pore adsorbents via novel modified U curve method

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A B S T R A C T

Proper estimation of pore size distribution (PSD) for various solid adsorbents is essential for efficient characterization of such materials. PSD determination is inherently an ill-posed problem which can be solved by resorting to Tikhonov regularization technique. Automatic selection of the optimal regularization level is crucial for efficient extraction of PSD from experimental adsorption or condensation isotherms. A detailed comparison of Leave One Out Cross Validation, L-curve, U-curve and modified L-curve criteria are presented using several real adsorption and condensation case studies. A modified U-curve criterion is also proposed and its superior performances are thoroughly validated. The new method employs a relatively simple minimization procedure, which is much easier than quite complex and tedious procedures used by conventional methods to compute their internal optimum parameters. Other practical issues, such as efficient computation of L-corner have been received proper attention in this article and a simple algorithm is presented for this purpose.

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Keywords: Pore size distribution; Regularization; LOOCV; L-curve; U-curve

1. Introduction

In many industrial applications, the adsorption force is dispersive by its nature and micro pore size distribution plays an important role in description of solid heterogeneity (Do, 1998). Two novel algorithms of SHN1¹ and SHN2² (based on inverse theory and Tikhonov regularization technique³) were previously presented in our recent articles for efficient and reliable estimation of pore size distribution (PSD) of nano-structured adsorbents using condensation and/or adsorption isotherms (Shahsavand and Niknam Shahrak, 2011a,b). As it was clearly shown in those articles, automatic selection of regularization parameter is crucial for successful extraction of PSD from measured noisy isotherms. Leave One Out Cross Validation criterion and various versions of L-curve and

U-curve methods are traditionally used for optimal selection of the regularization level (Amato and Hughes, 1991; Mc Carthy, 2003; Kunicke et al., 2005; Sourbron et al., 2004; Abascal et al., 2008; Krawczyk-stańdo and Rudnicki, 2007; Chiang et al., 2004). Some advantages and disadvantages about using the regularization technique can be found elsewhere (Arnrich et al., 2011)

Golub et al. (1979) presented a relatively simple method for fast calculation of optimal ridge regression parameter via generalized cross validation (GCV) criterion by resorting to singular value decomposition technique. Golub and Van Loan (1996) provided a more rigorous analysis regarding Leave One Out Cross Validation (LOOCV) criterion for ridge regression problem. Shahsavand (2000) provided a detailed mathematical derivation along with the use of generalized

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¹ Stands for Shahsavand–Niknam first method.

² Stands for Shahsavand–Niknam second method.

³ Also known as: Phillips–Twomey method, constraint linear inversion method and Tikhonov–Miller regularization.

singular value decomposition (GSVD) technique to extend the above approaches for higher orders of Tikhonov regularization procedure. Numerous applications of LOOCV criterion for optimal selection of regularization levels have been addressed in our previous works (Shahsavand and Niknam Shahrak, 2011a,b; Shahsavand and Ahmadvpour, 2005; Shahsavand and Pourafshari Chenar, 2007; Shahsavand, 2009). It was clearly shown that the LOOCV criterion may dramatically fail in some situations (Shahsavand and Niknam Shahrak, 2011a,b).

Using an entirely different approach, the L-curve criterion was initially presented by Lawson and Hanson (Lawson and Hanson, 1995). More recently, this technique was used by Hansen and O'Leary (Hansen, 1992; Hansen and O'Leary, 1993) to select the optimum value of regularization parameters for several numerical examples. Calvettia et al. (2000) reviewed various iterative procedures for determination of optimal regularization level by resorting to the L-curve criterion.

Automatic prediction of the so called L-corner is a major challenge for prediction of the optimal regularization level via L-curve criterion. Castellanos et al. (2002) proposed a triangle method (TM) for finding the corner of the L-curve. Numerical results on the collection of test problems were given to illustrate the potentiality of the method. They reported that, although the corner could not be exactly found in some cases, however, other neighbouring points on the L-curve were obtained which produced a good solution.

In 2005 and in an extensive research, Herdes et al. (2005a) presented a methodology based on combination of Grand Canonical Monte Carlo simulations, regularization procedure and singular value decomposition (SVD) technique to obtain PSD from experimental adsorption isotherms. They used discrete Picard condition (DPC) and L-curve (LC) criteria to find the PSD of a plugged hexagonal template silica (PHTS). In the same year and in a similar article, Herdes et al. (2005b) used exactly the same approach to find the PSD of various adsorbents assuming cylindrical geometry for all porous materials. Once again the LC criterion was employed for optimal selection of zero order regularization parameter.

Morigi et al. (2006) explored how the guidelines developed within the context of asymptotic expansions can be applied to iterative methods for solution of ill-posed problems. They used the L-curve criterion to determine a subset of consecutive iterates associated with the points in a neighborhood of the vertex of the L-curve. They remarked that the use of L-curve may not guarantee to give the best approximant.

In 2004, Hansen et al. (2007) submitted an article (published in 2007) which described an adaptive implementation of the L-curve criterion. The algorithm locates the corner of a discrete L-curve on a log-log scale and does not require any predefined parameter to capture the global features of the curve in an adaptive fashion. They used a sequence of pruned L-curves by considering the curves at different scales. They concluded that "the heuristic L-curve algorithm can fail no matter how it is implemented" (Hansen et al., 2007).

Santos and Bassrei (2007) used both L- and θ -curve approaches for the optimal selection of regularization parameter in geophysical diffraction tomography. The detection of the L-curve corner was performed using Hansen's toolbox. For the first time, non-zero orders of regularization were used to construct the L-curve. An interesting interpretation of the L-curve was presented by dividing it into two distinct regions of smaller error and smoother solution. They introduced θ -curve criterion based on a curve representing the cosine of angles between adjacent segments of L-curve discrete

representation. Santos and Bassrei also used several synthetic data sets to compare the performances of zero, first and second order regularization techniques with each other.

Krawczyk-stańdo and Rudnicki (2007) proposed the U-curve criterion for selection of the regularization parameter (λ). They also compared the new criterion with traditional L-curve method using several numerical examples and concluded that "it works well in practice" (Krawczyk-stańdo and Rudnicki, 2007).

Reichel and Sadok (2008) proposed a new L-curve heuristic to determine the optimal level of regularization for ill-posed problems via the truncated singular value decomposition (TSVD) technique. The truncation index was determined by how well the given data can be approximated by a linear combination of the first singular vectors or functions. They concluded that "the residual L-curve also can be applied in conjunction with other solution methods than TSVD, such as with iterative methods, extrapolation methods, and multi-parameter methods".

Rezghi and Hosseini (2009) introduced a new variant of L-curve to estimate the zero order regularization parameter for the solution of discrete ill-posed problems. They used the vertex of Euclidean norm of solution vectors versus square of regularization parameter (λ^2) to determine the optimum level of regularization. The L-corner was also predicted using curvature variations instead of curvature via a newly proposed correlation.

Heng et al. (2010) proposed a novel approach for the modified L-curve method to replace the residual norm and the regularized solution norm with other model functions. Several Lemmas and theorems were proved to verify this issue. The new approach was reported to be less computational demanding compared to traditional L-curve method. The performance of the proposed technique was tested using an inverse heat conduction problem (IHCP).

In the present article, a brief overview of our recently proposed methods (SHN1 and SHN2) for PSD recovery of heterogeneous adsorbents from condensation and adsorption data sets via inverse theory will be presented. The regularization technique will be used to stabilize the solution of ill-posed adsorption problem. Various criteria such as LOOCV, L-curve (LC), modified L-curve (MLC), U-curve (UC) and our new method (the so-called Modified U-curve (MUC)) will be described in more details for automatic selection of optimal regularization parameters. The performances of these criteria will be thoroughly compared together by using various condensation and adsorption experimental data sets borrowed from literatures (Solcova et al., 2006; Kowalczyk et al., 2005; Moellmer et al., 2010). A simple algorithm is also presented for computation of L-corner. Ultimately, it's worthwhile to mention that the validation of the SHN1 and SHN2 methods by synthetic data rather than real cases, has been completely implemented in our two previously published articles (Shahsavand and Niknam Shahrak, 2011a,b). So here we will examine these two methods along our proposed Modified U-curve criterion just for experimental data sets.

2. A brief review of SHN1 and SHN2 methods

Two novel methods of SHN1 and SHN2 were presented in our recent articles 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 been received sufficient attention in those articles (Shahsavand and Niknam Shahrak, 2011a,b). A brief overview will be presented in the following sections 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 ; $i = 1, \dots, n$):

$$\psi(P_i) = \int_0^{r_k(P_i)} f(r) dr \quad (\text{mere condensation}) \quad (1)$$

$$\psi(P_i) = \int_0^{r_k(P_i)} f(r) dr + t \int_{r_k(P_i)}^{\max} \frac{2f(r)}{r} dr. \quad (\text{condensation with a prior adsorbed layer}) \quad (2)$$

Similarly, as shown below, the B matrices have two or three rows fewer than their columns when second or third orders of regularization are employed.

$$B = \begin{bmatrix} -1 & 2 & 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 1 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & -1 & 2 & 1 \end{bmatrix} \quad (4)$$

$$B = \begin{bmatrix} -1 & 3 & -3 & 1 & 0 & 0 & 0 \\ 0 & -1 & 3 & -3 & 1 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & -1 & 3 & -3 & 1 \end{bmatrix} \quad (5)$$

This procedure can be continued to construct the corresponding B matrices for higher orders of regularizations. For example, for eighth order of regularization, the B matrix has eight rows fewer than its columns and can be easily computed as:

$$B = \begin{bmatrix} -1 & 8 & -28 & 56 & -70 & 56 & -28 & 8 & -1 & 0 & \dots & 0 \\ 0 & -1 & 8 & -28 & 56 & -70 & 56 & -28 & 8 & -1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & -1 & 8 & -28 & 56 & -70 & 56 & -28 & 8 & -1 & 0 \\ 0 & \dots & 0 & -1 & 8 & -28 & 56 & -70 & 56 & -28 & 8 & -1 \end{bmatrix} \quad (6)$$

The above ill-posed problems of finding $f(r)$ from above integrals can be replaced with a set of linear algebraic equations $\{(R^T R + \lambda B^T B) \underline{f}(r) = R^T \underline{\psi}\}$, using a combination of inverse theory and linear regularization technique. In this equation, the $N \times M_t$ coefficient matrix⁴ $R \in \mathbb{R}^{[N \times \sum_{i=1}^N M(P_i)]}$ has usually many more columns than its rows (depending on the order of regularization technique used), the overall PSD column vector ($\underline{f} \in \mathbb{R}^{[\sum_{i=1}^N M(P_i) \times 1]}$) has dimensions of $[\sum_{i=1}^N M(P_i) \times 1]$, $\underline{\psi}$ is a $[N \times 1]$ vector and λ is the regularization parameter. Detailed descriptions of various R matrices corresponding to Eqs. (1) and (2) has been presented elsewhere (Shahsavand and Niknam Shahrak, 2011a,b).

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 $I \in \mathbb{R}^{[\sum_{i=1}^N M(P_i) \times \sum_{i=1}^N M(P_i)]}$. For first order regularization, the double band matrix B has one fewer rows than its columns.

$$B = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & -1 & 1 \end{bmatrix} \quad (3)$$

⁴ $M(P_i)$ 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.

After construction of matrix R and using 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 $f(r)$. Various criteria (e.g. LOOCV, LC, UC and MLC) have been used in literatures for automatic selection of optimum regularization parameter (λ^*). The following section provides a brief review of such criteria (along with our new proposed method (MUC)) accompanied with several experimental test examples to investigate the performance of each criterion.

3. Automatic selection of regularization parameter

Various ill-posed inverse problems are frequently encountered in many practical engineering assignments. Linear regularization technique is usually employed to stabilize the solution of such ill-posed inverse problems (Press et al., 1992). As mentioned earlier, combination of inverse theory and linear regularization technique reduces the solution of integral equations of (1) and (2) to the solution of the following linear sets of algebraic equations:

$$(R^T R + \lambda B^T B) \underline{f}(r) = R^T \underline{\psi} \quad (7)$$

Visual selection of optimization level is inconvenient and reliable techniques are required for automatic selection of regularization parameter. The following sections briefly review various optimization techniques available to tackle this issue. Fifteen practical experimental data sets are used to investigate the performances of each criterion. Only the most successful or failed performances are presented for each case.

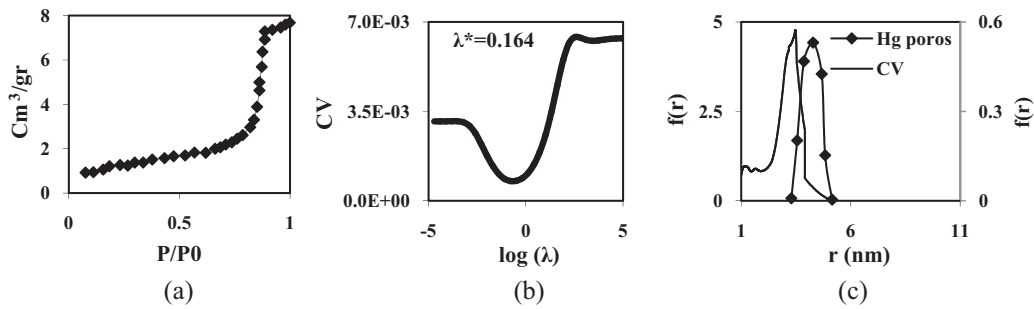


Fig. 1 – (a) N_2 adsorption isotherm on CPG75 adsorbent at 77 K, (b) variations of LOOCV with λ and (c) comparison of extracted PSD (left) with the real PSD (right).

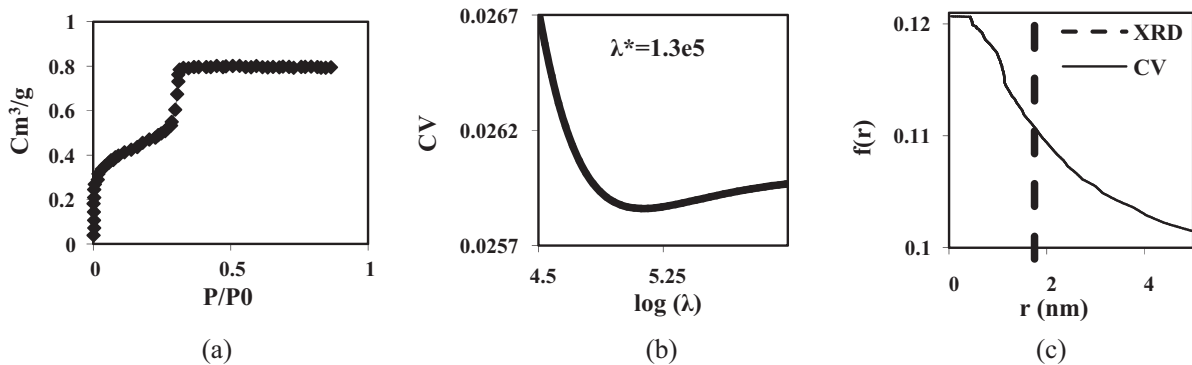


Fig. 2 – (a) N_2 adsorption isotherm on MCM-C14 adsorbent at 77 K, (b) variations of LOOCV with λ and (c) comparison of extracted PSD (CV) with the real PSD (XRD).

3.1. Leave One Out Cross Validation (LOOCV) method

Golub and Van Loan (1996) presented the following equation to find the Leave One Out Cross Validation (LOOCV) criterion.

$$CV(\lambda) = \frac{1}{N} \sum_{k=1}^N \left[\frac{e_k^T [I_N - H(\lambda)] y}{e_k^T [I_N - H(\lambda)] e_k} \right]^2 \quad (8)$$

$$H(\lambda) = R(R^T R + \lambda B^T B)^{-1} R^T \quad (9)$$

The optimal value of regularization parameter can be selected by minimization of the above merit function. Evidently, the inversion of $M \times M$ matrix $\{(R^T R + \lambda B^T B)\}$ at each value of λ requires an order of $((M \times M)^3)$ mathematical operations which is extremely time demanding. This problem can be solved by resorting to the generalized singular value decomposition (GSVD) technique which transforms Eq. (8) to the following formula⁵:

$$CV(\lambda) = \frac{1}{N} \sum_{k=1}^N \left[\frac{y_k - \sum_{j=1}^r (u_R)_{kj} [(d_{R_j}^2) / (d_{R_j}^2 + \lambda d_{B_j}^2)] b_j}{1 - \sum_{j=1}^r (u_R)_{kj}^2 [(d_{R_j}^2) / (d_{R_j}^2 + \lambda d_{B_j}^2)]} \right]^2 \quad (10)$$

where, $\underline{b} = U^T y$ and r is the effective rank of $(R^T | B^T)^T$. This criterion can provide correct value of optimal regularization level (λ^*) for many practical situations. Fig. 1 shows a typical example of such situation when LOOCV criterion is successfully used along with SHN1 method to determinate the optimal PSD of a porous adsorbent from a condensation data set.

Fig. 1(a) illustrates the nitrogen adsorption isotherm of CPG⁶ 75 adsorbent at 77 K, borrowed from literature (Solcova et al., 2006). Fig. 1(b) demonstrates the variations of LOOCV criterion with regularization parameter and Fig. 1(c) shows the comparison of optimal PSD extracted at ($\lambda^* = 0.164$) with the actual PSD obtained from mercury porosimetry. Evidently, the LOOCV criterion performs an outstanding and impressive job on recovery of PSD from experimental isotherm using SHN1 method.

Unfortunately, LOOCV criterion does not perform so adequately for all cases. Fig. 2 shows a dramatic failure of this criterion when applied to SHN2 method for extraction of PSD from a set of real adsorption data. Fig. 2(a) illustrates the nitrogen adsorption isotherm on MCM⁷-C14 adsorbent at 77 K borrowed from (Kowalczyk et al., 2005). Fig. 2(b) shows the variations of LOOCV criterion with λ and Fig. 2(c) presents the drastically failed performance of SHN2 method at optimal level of regularization ($\lambda^* = 1.3e5$) predicted by LOOCV criterion. The dashed line of Fig. 2(c) shows the real PSD of adsorbent obtained from XRD⁸ method.

It is interesting to note that the SHN2 method can perform very adequately when proper value of regularization parameter (determined by visual method or other techniques such as LC, UC or modified LC) is used. Fig. 3 provides the successful extraction of PSD from the same data set of Fig. 2, when proper level of regularization ($\lambda^* = 0.0205$) is employed. Obviously, visual confirmation is not possible for practical cases (when the actual PSD is not known) and other reliable techniques are required for automatic selection of the optimal regularization level. The next section describes some of these

⁵ Detailed mathematical derivation of this equation is presented in reference (Golub and Van Loan, 1996).

⁶ Controlled-pore glasses.

⁷ Mesopore carbon material.

⁸ X-ray diffraction.

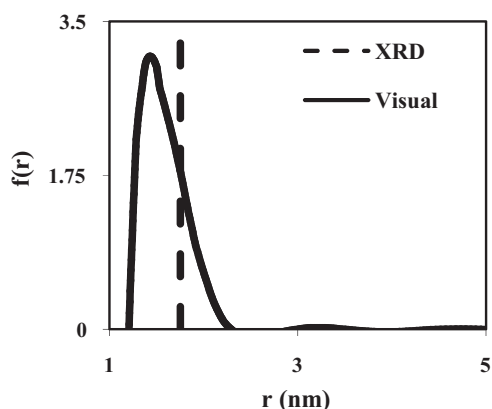


Fig. 3 – Impressive performance of SHN2 on PDS recovery of MCM-C14 using optimal value of regularization parameter obtained via visual technique.

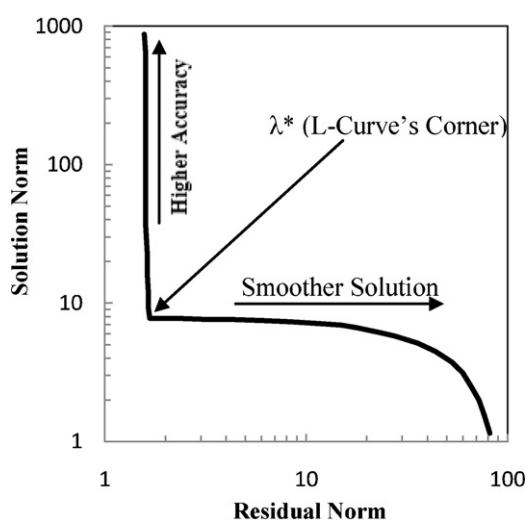


Fig. 4 – Schematic representation of L-curve.

more successful techniques. Furthermore, we have to mention that real or actual PSDs usually are extracted via methods that do not require any adsorption isotherms and or do not include any unrealistic assumptions. These methods that we name them as independent methods, like Hg-porosimetry and or X-ray diffraction, can be employed to calculate the pore size of adsorbents (Solcova et al., 2006).

3.2. L-curve method

The so called L-curve criterion has gained many attentions in the last couple of decades for selection of optimal values of Tikhonov regularization parameter (Lawson and Hanson, 1995; Miller, 1970; Tikhonov, 1963). The L-curve was originally a plot (almost always in log–log scale) of corresponding values of the solution and residual norms (defined by Eqs. (11) and (12)) parameterized by the zero order regularization parameter.

$$\gamma(\lambda) = \|\hat{u}\|^2 = u^T u \quad (11)$$

$$\xi(\lambda) = \|\hat{R}\hat{u} - y\|^2 = (\hat{R}\hat{u} - y)^T (\hat{R}\hat{u} - y) \quad (12)$$

This curve is constructed by connecting discrete points and in most cases exhibits a typical “L” shape. The optimal value of the regularization parameter (λ^*) is considered to be the one corresponding to the corner of such “L”, as shown in Fig. 4.

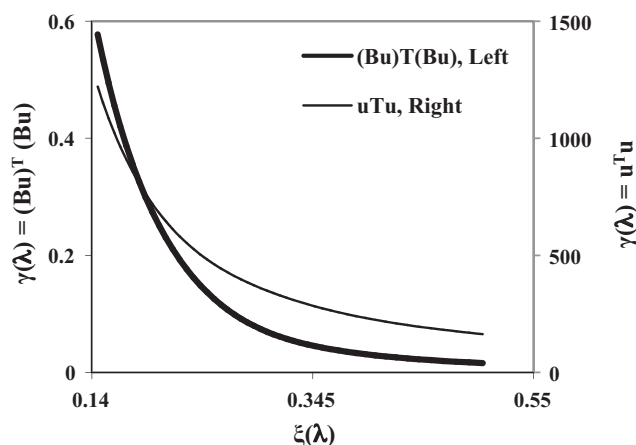


Fig. 5 – Plot of Eqs. (11) and (13) when first order regularization is used.

The left side of L-curve is nearly a vertical line and any point on this side of L-curve provides better accuracy with poor smoothness. Correspondingly, the right side offers less accurate solution but fairly proper smoothness is expected. L-curve corner represents a trade-off between smoother solutions with poor accuracy and rougher solutions with more appropriate precision (Santos and Bassrei, 2007).

Since in many previous case studies, zero order regularization methods are used, therefore Eq. (11) defines the solution norm. When higher orders of regularization are attempted, the so called solution norm should be computed from the following equation.⁹

$$\gamma(\lambda) = \|B\hat{u}\|^2 = (Bu)^T (Bu) \quad (13)$$

where B matrix is already defined in Eqs. (4)–(6). Fig. 5 illustrates both L-curves of solution norms computed via Eqs. (11) and (13) versus the residual norm of Eq. (12), when first order regularization technique is applied to the isotherm of MCM-14 (see Fig. 2). It should be emphasized that the solution norm ($u^T u$) belongs to the first order regularization (and not to zero order regularization) technique. Evidently, Eq. (13) provides better L-shapes, which enhances the automatic selection of the so called L-corner. In all coming examples, Eq. (13) will be used to define the solution norm $\gamma(\lambda)$.

After plotting the L-curve, automatic selection of the L-corner is a major challenge and as it will be reviewed briefly in the next section, several techniques have been presented to tackle this issue.

3.2.1. Automatic detection of L-corner

Visual selection of L-corner is the quite simple and relatively less time consuming but the optimum value of regularization parameter obtains by this method usually is not very accurate and it can be used for initialization purposes. Other methods are developed for automatic selection of the L-corner which for the sake of brevity only two of them will receive proper attention in this section.

3.2.1.1. Hansen method. One of the most widely used methods for selection of L-corner was originally proposed by

⁹ The residual norm should be still computed via equation (12).

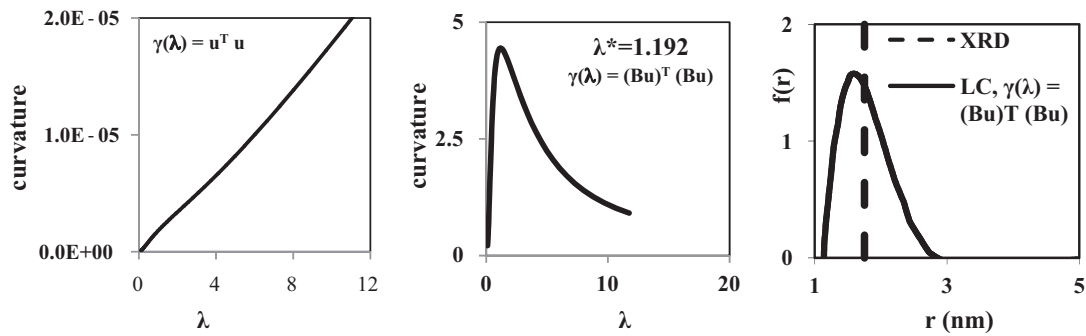


Fig. 6 – Comparison of recovered PSDs when different definitions are used for $\gamma(\lambda)$.

Hansen and O’Leary (1993). This method finds the corner of L-curve by resorting to maximum curvature concept. Hansen and O’Leary proposed the following equation to calculate the curvature of L-curve at any given level of regularization¹⁰ (Hansen and O’Leary, 1993):

$$k(\lambda) = \left(\frac{d\xi\gamma - d^2\xi d\gamma}{((d\xi)^2 + (d\gamma)^2)^{1.5}} \right) \quad (14)$$

Hansen also proposed a more convenient equation which does not require second derivatives (d^2) for calculation of L-curve curvature¹¹ (Hansen, 2001):

$$k(\lambda) = 2 \left(\frac{\gamma\xi}{d\gamma} \right) \left(\frac{\lambda^2 d\gamma\xi + 2\lambda\gamma\xi + \lambda^4 \gamma d\gamma}{((d\gamma)^2 + \xi^2)^{1.5}} \right) \quad (15)$$

Instead of using the differentiations with respect to λ , one may compute the curvature by direct differentiations of $y=f(x)$ versus (x) .¹²

$$k(\lambda) = \frac{y''}{(1 + (y')^2)^{1.5}} \quad (16)$$

Evaluation of L-corner curvature via Eqs. (14)–(16) is extremely time demanding for large collections of regularization levels. Initially, two models should be fitted to the curves of γ and ξ versus λ and then the required differentiations should be evaluated. In most cases, the fitted equations are complex and cannot be easily differentiated. In such situations, numerical differentiations should be used which are less accurate and have their own limitations. Another stronger difficulty arises when the measured data is contaminated with appreciable amount of noise which is the dominant case in many engineering problems such as determination of pore size distribution of an adsorbent from noisy isotherms (Hansen, 2001). This problem usually leads to over prediction of optimal regularization parameter.¹³

¹⁰ Where d and d^2 denote the first and second differentiations with respect to λ , respectively.

¹¹ Hansen and O’Leary also presented two additional algorithms for selection of L-corner when other special cases are encountered (Hansen, 1992).

¹² Where y' and y'' denote the first and second derivatives of y with respect to x , respectively.

¹³ As will be shown later in Fig. 6(b).

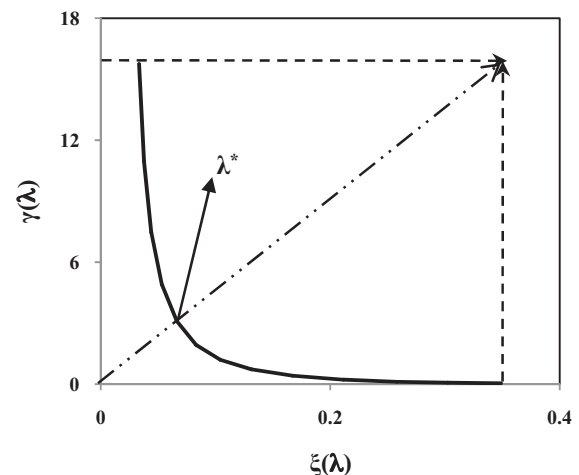


Fig. 7 – A typical schematic diagram of the newly proposed method.

Fig. 6 shows the curvatures of the L-curves computed by Eqs. (11) and (13) and plotted against residual norm defined via Eq. (12). As it was expected, the curvature of L-curve based on $\gamma(\lambda) = u^T u$ fails drastically for first order linear regularization, while similar L-curve based on $\gamma(\lambda) = Bu^T Bu$ shows a perfect maximum which recovers PSD very close to experimental value.

Although, there are several other methods (such as: the point closest to an origin point (Belge et al., 1998) or the point of tangency with a straight line of negative slope (Reginska, 1996)) in the literature which may provide L-corner, however, the Hansen method of finding L-corner based on calculation of L-curve curvature is more popular. A more convenient technique is presented in the next section which can successfully provide the L-corner with a much simpler procedure.

3.2.1.2. A Novel method for determination of the corner of L-curve. In our new approach, the L-corner is simply computed by intercepting the L-curve with a line connecting origin to the extreme point. As shown in Fig. 7, the horizontal component of the so called extreme point equals to the maximum value of x axis and its vertical component is identical with the maximum value of y axis. Fig. 8(b) shows that our very convenient method locates much better the L-corner compared to the relatively complex method of Hansen (Eq. (14) or (15)), when the L-curve appreciably deviates from L-shape. In other situations, as shown in Fig. 8(a), both methods predict the same point for L-corner.

To investigate the effectiveness of L-curve criterion on recovery of PSD from a real isotherm, the example of Fig. 2

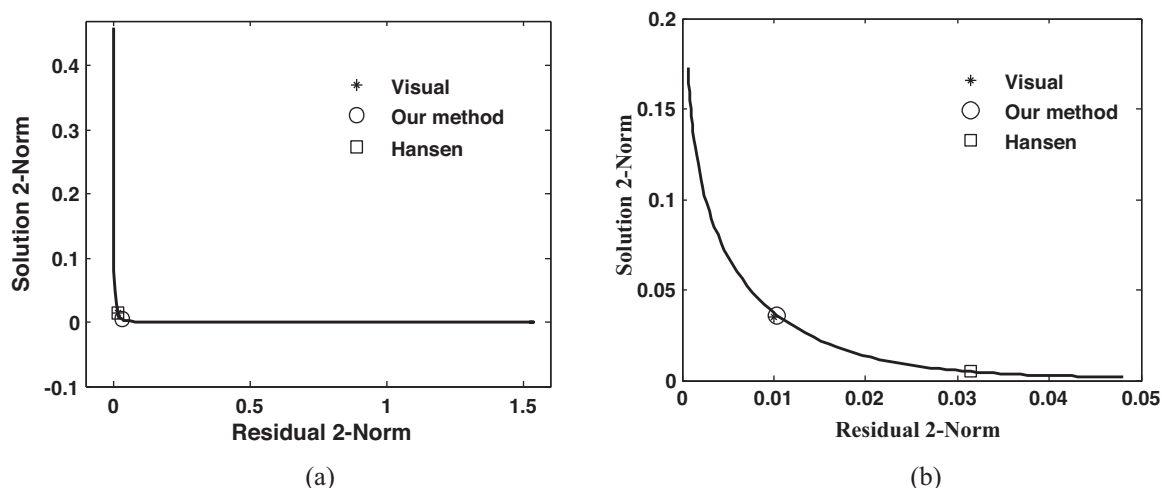


Fig. 8 – (a) L-curve exhibits L-shape (both methods are successful), (b) L-curve deviates L-shape (our method succeeds while Hansen method fails to predict the L-corner).

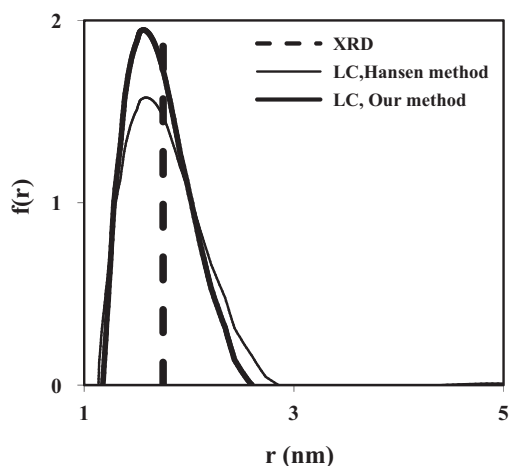


Fig. 9 – Comparison of Hansen method and our presented algorithm for selection of L-corner on PSDs recovery of MCM-C14.

is used again. As it was shown earlier, LOOCV criterion could not provide the correct value of the optimal regularization parameter. Fig. 9 illustrates the recovered PSDs, when Hansen method and our new simple algorithm are used for L-corner prediction. Although the optimum regularization levels are slightly different from each other,¹⁴ however, both methods perform very adequately and can extract the correct PSD from the isotherm of Fig. 2 using first order regularization technique. A task, which has been dramatically failed by LOOCV criterion (see Fig. 2).

Although, L-curve criterion equipped with our L-corner selection technique (which is more convenient than the complex maximum curvature calculation procedure of Hansen and O’Leary) usually provides better performance than LOOCV criterion for optimal selection of regularization levels, However, it may fail in some practical applications as shown in reference (Vogel, 1996). For this reason, other criteria will be addressed in the next section for more reliable prediction of optimal regularization levels.

3.3. U-curve method

Krawczyk-stańdo and Rudnicki (2007) proposed the so called U-curve criterion for reliable estimation of optimal regularization parameter based on the following equation.

$$U(\lambda) = \frac{1}{\xi(\lambda)} + \frac{1}{\gamma(\lambda)} \quad (17)$$

Here, $\xi(\lambda)$ and $\gamma(\lambda)$ are defined by Eqs. (12) and (13) and denote the solution and residual norms at any given level of regularization parameter (λ). The U-curve is simply a plot of $U(\lambda)$ (defined by Eq. (17)) versus regularization parameter (λ). In many real case studies, this curve exhibit typical “U” shapes and optimum regularization parameter λ^* should be computed by finding a point in which the curvature attains a local maximum (preferably) close to the left vertical part of the U-curve (Krawczyk-stańdo and Rudnicki, 2007). Fig. 10 shows the U-curve computed for MCM-C14 adsorbent of Fig. 2 and its successfully predicted PSD at optimum level of regularization ($\lambda^* = 0.161$).

As shown in Fig. 11(b), in many real situations the original U-curve plot may not provide a distinct minimum. In such cases, the magnification of the U-curve plot around the U-corner may show a distinct U-shape with a clear minimum. Adsorption isotherm of nitrogen on CPG 159 adsorbent at 77 K (borrowed from (Solcova et al., 2006) and shown in Fig. 11(a) is used to address this issue. Fig. 11(b)–(d) provides the original and magnified U-curves, corresponding curvature plots versus λ and the recovered PSD at λ^* obtained by pinpointing the maximum curvature of magnified U-curve.

As it is clearly illustrated in Fig. 11(c), the curvature of original U-curve (thin line) is monotonic and does not provide a distinct maximum. On the other hand, the curvature of magnified U-curve (thick line) shows a perfect maximum in which the corresponding λ^* recovers the optimal PSD from SHN1 method very close to the real PSD obtained from Hg porosimetry (borrowed from (Solcova et al., 2006)).

For this specific example, the optimal regularization level computed via maximization of magnified U-curve curvature (Fig. 11(c)) is the same as λ^* obtained by minimization of Magnified U-curve (Fig. 11(b)). Evidently, minimization of a convex univariate function is much simpler than the tedious and time consuming curvature calculations for

¹⁴ $\lambda^* = 1.192$ for Hansen method and $\lambda^* = 0.35$ for our algorithm

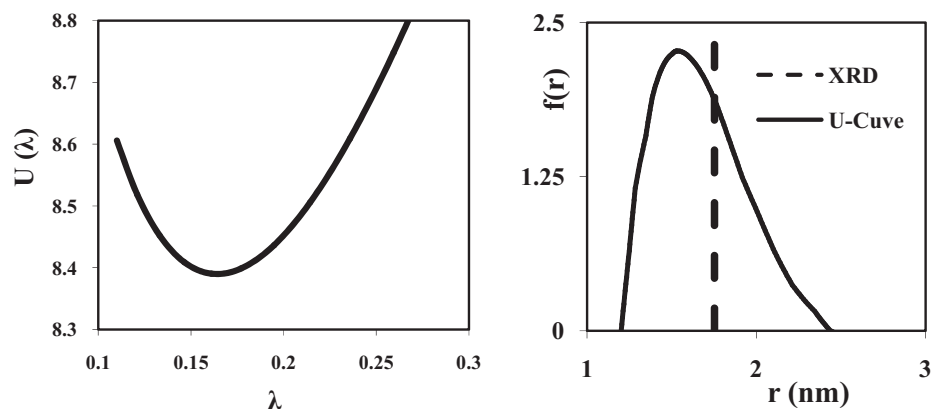


Fig. 10 – Computed U-curve for MCM-C14 and corresponding optimally recovered PSD.

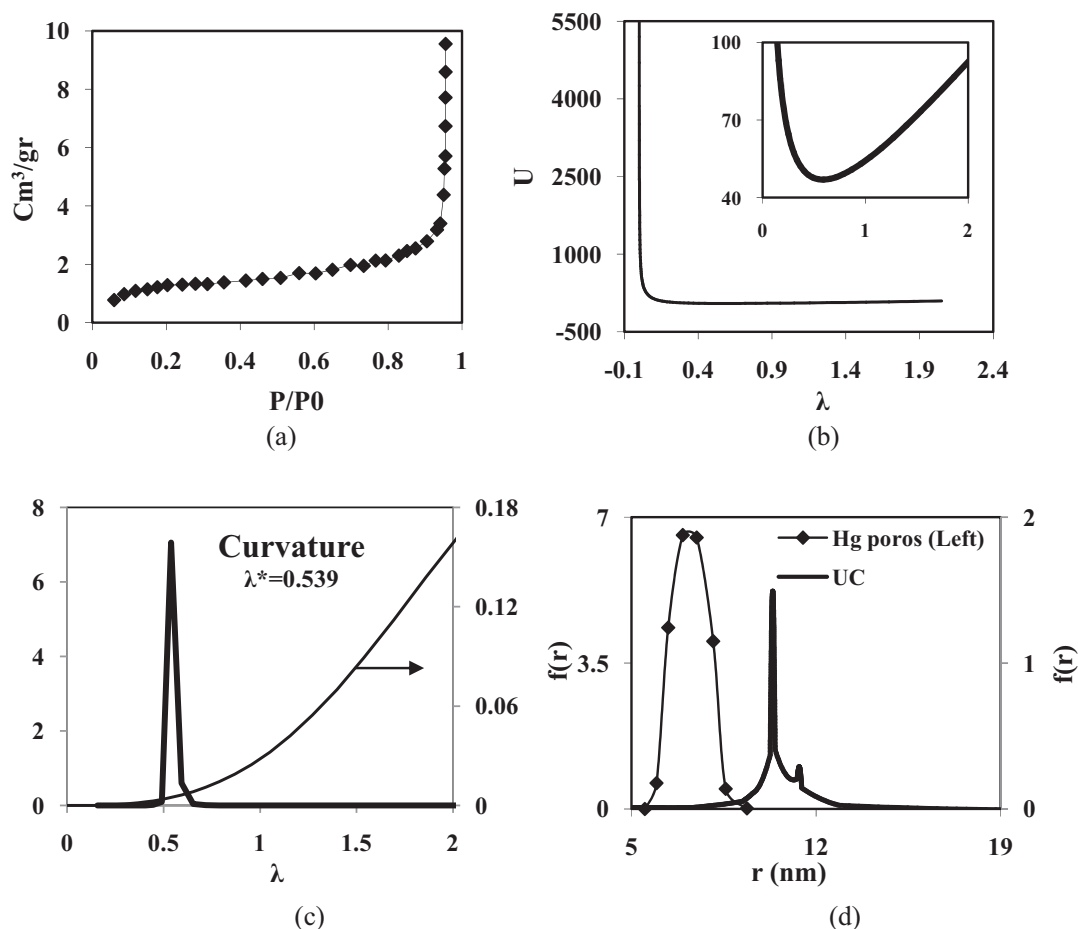


Fig. 11 – (a) Nitrogen adsorption isotherm on CPG159, (b) original and magnified U-curves, (c) curvature plots of both U-curves and (d) Optimally recovered PSD based on magnified U-curve.

selection of proper λ^* . Unfortunately, this issue may not be true in all other cases, especially when the U-curve exhibits a vertical–horizontal–vertical feature. In such cases, the optimal point usually lies near the left leg of U-curve (Krawczyk-stańdo and Rudnicki, 2007).

As shown in Fig. 12 for adsorption of argon at 87.3 K on a typical Metal-Organic Framework (MOF) adsorbent (Moellmer et al., 2010), the U-curve plot actually exhibits a monotonic (rising or falling) characteristics which does not provide a maximum curvature. In such cases, the U-curve method dramatically fails and other more efficient techniques (such as modified L-curve method) are required to provide the optimum level of regularization.

3.4. Modified L-curve method

Rezghi and Hosseini (2009) modified the L-curve (MLC) method by plotting the solution norms (defined by Eq. (13)) versus square of regularization parameters λ^2 . In most cases, this curve exhibits a typical “L” shape, and the optimal value of the regularization parameter λ^* is considered to be the one corresponding to the corner of the “L”. They also proposed a new algorithm for selection of the corner of modified L-curves based on curvature variations. It was shown that the curvature variation method provides better means of determining optimal regularization level (λ^*) than traditional curvature plot (Rezghi and Hosseini, 2009). Variation of curvature between

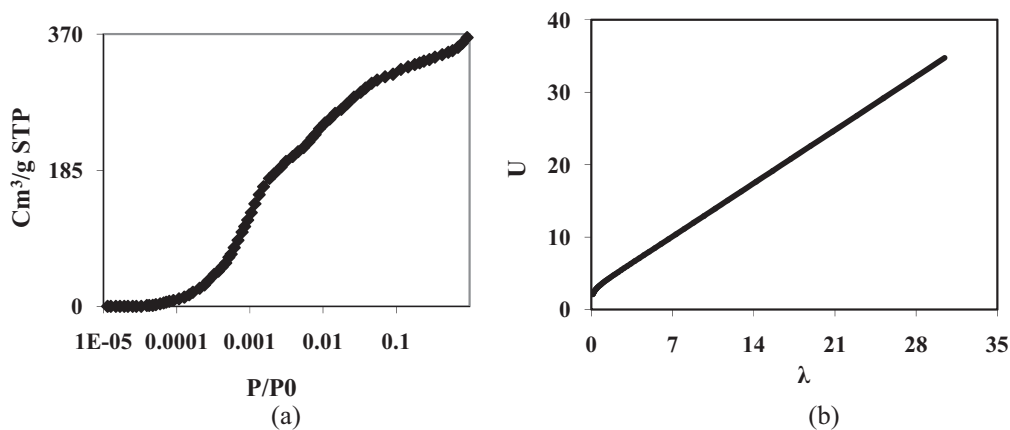


Fig. 12 – (a) Argon adsorption isotherm on Soc-MOF adsorbent and (b) failed U-curve.

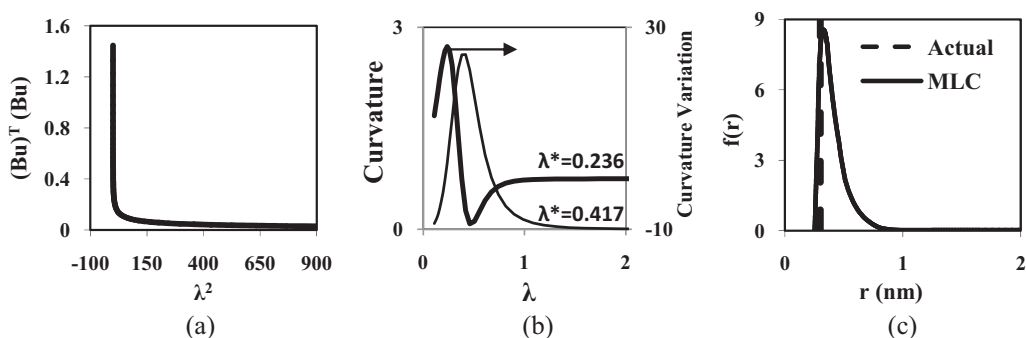


Fig. 13 – (a) Modified L-curve for isotherm of Fig. 12(a), (b) curvature and curvature variation plots and (c) very impressive recovered PSDs.

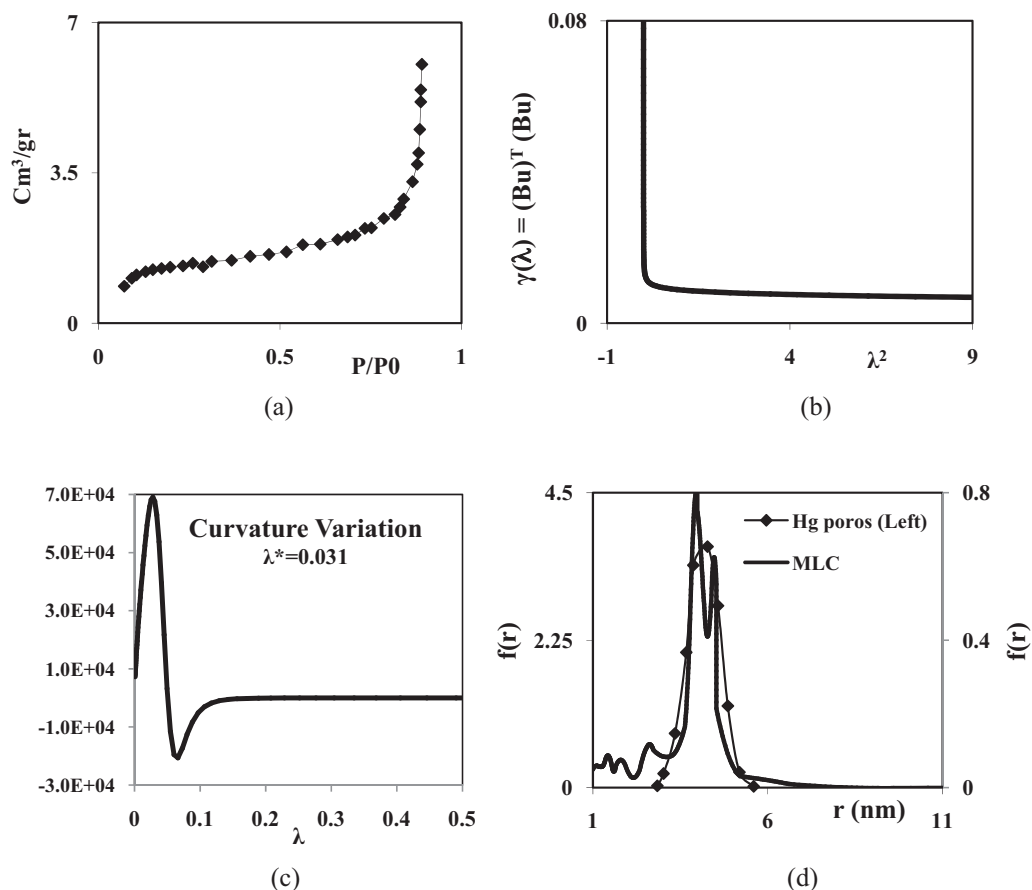


Fig. 14 – (a) Nitrogen adsorption isotherm on CPG80 at 77 K (Solcova et al., 2006), (b) Modified L-curve, (c) curvature variations plot and (d) PSD obtained via SHN1 method and real PSD.

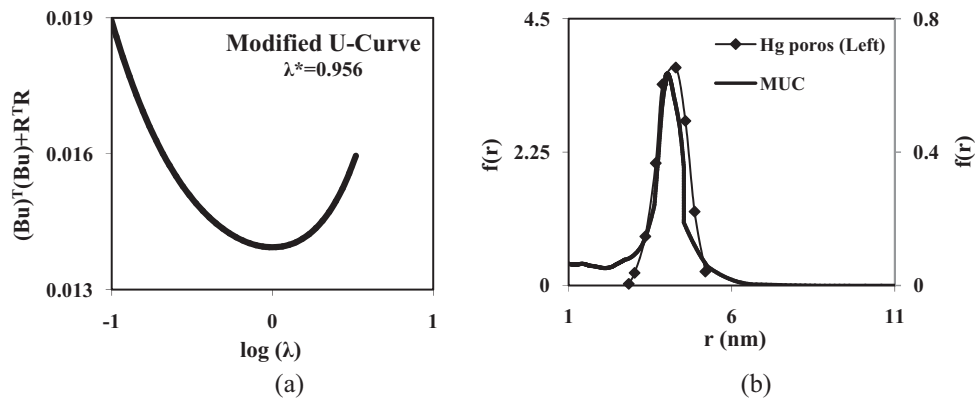


Fig. 15 – (a) Modified U-curve for CPG80 isotherm and (b) exactly recovered PSD.

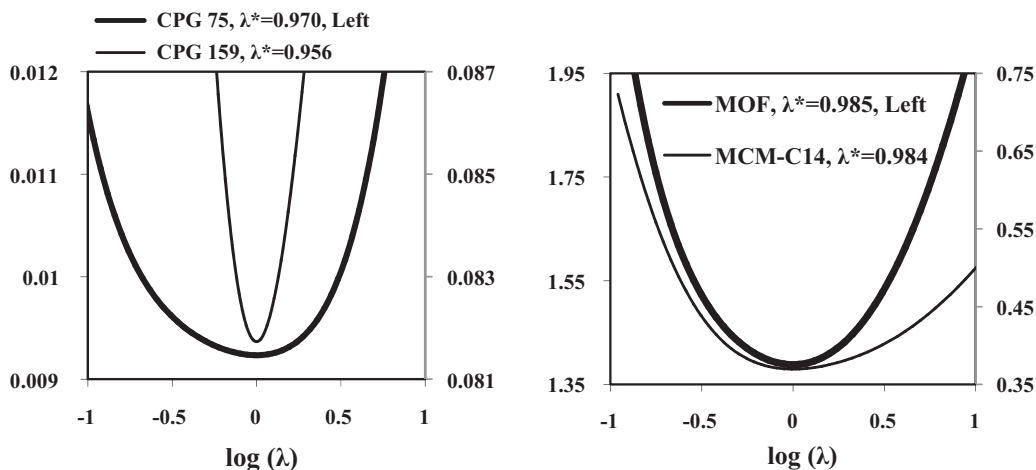


Fig. 16 – Various modified U-curves and their corresponding λ^* values.

two adjacent regularization parameters (λ_i, λ_{i+1}) should be computed as¹⁵:

$$v_i = \frac{k_{i+1} - k_i}{\lambda_{i+1}^2 - \lambda_i^2} \quad (18)$$

They also emphasized that the optimum value of regularization parameters (λ^*) corresponds to the point where the maximum variation in curvature occurs (Rezghi and Hosseini, 2009).

As it was shown in Fig. 12, the U-curve criterion failed to provide a point with a proper maximum curvature. Hence it is unable to offer a correct PSD for the adsorption data presented in Fig. 12(a). As it can be seen in Fig. 13, the application of modified L-curve (MLC) criterion provides two similar optimum regularization levels when curvature (left axis of Fig. 13(b), thin line) or curvature variations (right axis of Fig. 13(b), thick line) are maximized. Fig. 13(c) illustrates that both optimal levels of regularizations used by SHN2 method lead to a unique PSD which almost lies over the actual PSD obtained from X-ray diffraction (XRD). This impressive performance of the MLC criterion (among many others) show that such powerful technique when coupled with SHN1 or SHN2 methods can successfully used for optimal recovery of PSD from experimental isotherms.

MLC criterion suffers from computational demanding procedure of finding curvature and curvature variations for large

sets of regularization parameters. Moreover, as shown in Fig. 14 for adsorption of nitrogen over CPG 80 at 77 K (borrowed from (Solcova et al., 2006)), the predicted PSD (via SHN1) although correctly pinpoints the peak location, however, it may show some unrealistic multiple peaks.

3.5. Modified U-curve method

We define a new criterion based on modification of conventional U-curve. In this approach, the modified U-curve plot is constructed by plotting the summation of both solution and residual norms (Eq. (19)) versus logarithm of regularization parameter ($\log(\lambda)$).

$$MU(\lambda) = \xi(\lambda) + \gamma(\lambda) \quad (19)$$

Unlike traditional U-curve criterion which usually deviates from U-shape, the semi-log MUC plot is almost always lead to a U-shape curve with a distinct minimum. This new criterion was applied to the CPG 80 isotherm data of Fig. 14(a) using SHN1 method. As shown in Fig. 15, the optimum level of regularization (λ^*) found by minimization of MU plot, exactly recovers the actual PSD.

Evidently, finding the minimum of a univariate function is much simpler and more convenient than calculation of curvature or curvature variation. Therefore, the proposed method is extremely simple to use and to the best of our experience it never deviates from U-shape and always recovers appropriate PSD at optimum level of regularization.

¹⁵ The curvature (k) is computable via Eqs. (14)–(16).

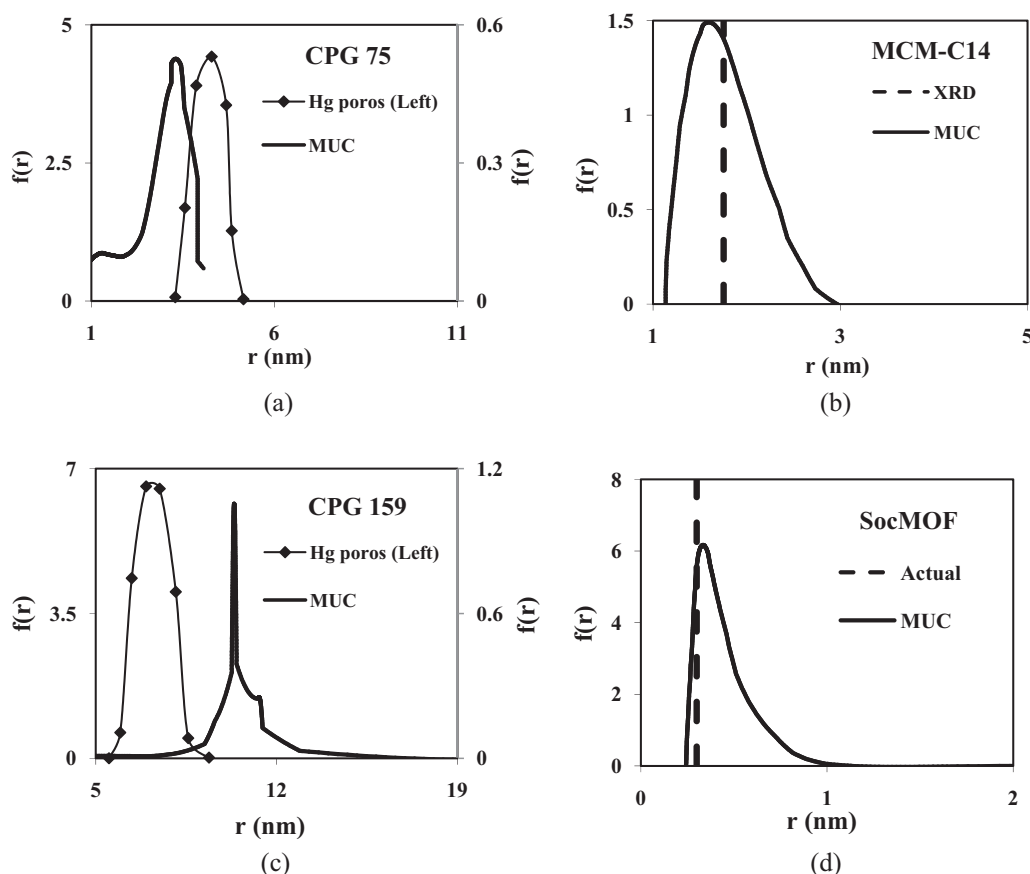


Fig. 17 – Remarkable performances of MUC criterion on PSD recovery of four different examples used throughout the entire article.

To emphasize this issue and to demonstrate the superior performances of our newly proposed criterion (MUC), it is applied to the entire sets of isotherm data used from the beginning of this article (among many others¹⁶). Fig. 16 clearly shows that for all of these data sets, the MUC criterion provides perfect U-curves with well-defined minima corresponding to different optimum regularization levels. Fig. 17 illustrates the impressive performances of our newly proposed technique (MLC) on recovery of PSD using the optimal regularization levels found in Fig. 16.

4. Conclusions

A new criterion (MUC) is presented for efficient and convenient estimation of optimal regularization level for the ill-posed inverse problem of finding PSD from isotherm data. This new criterion outperforms other conventional criteria such as Leave One Out Cross Validation (LOOCV), L-curve (LC), modified L-curve (MLC) and U-curve (UC). Several real case studies were used to compare the performances of all above criteria for estimation of optimal regularization parameter used in SHN1 and SHN2 methods as described in our recent articles). It was clearly shown that traditional criteria such as LOOCV and UC drastically fail in practice and can't provide proper values for optimal regularization parameter. The most important advantage of the new MUC criterion over LC and MLC criteria is its simplicity and its reliable

performance for estimation of λ^* . In all 15 cases considered in this study, the newly proposed method never fails and always provides proper optimal values for regularization problem which successfully recovers PDS compared to experimental XRD or mercury porosimetry distributions. Furthermore, an easy procedure is presented in Section 3.2 for reliable prediction of L-corner.

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¹⁶ Other than these four examples, MLC criterion was also tested for ten other real case studies. It performed very adequately on PSD recovery of all adsorbents.

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