Sensitivity Analysis of Adsorption Isotherms Subject to Measurement Noise in the Data

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Abstract

The analysis and design of many environmental and separation processes rely on the availability of accurate adsorption isotherms. These isotherms are estimated from measurements of the adsorption process variables. Unfortunately, these variables are usually contaminated with errors that affect the accuracy of their estimated parameters. Therefore, one objective of this work was to study the effect of measurement noise in the variables on the estimation accuracy of the Langmuir isotherm. In fact, Langmuir has three linearized forms, so it was sought to determine which out of these three forms would provide the most accurate estimated parameters. Another objective of this work was to estimate the isotherm parameters using the nonlinear Langmuir form using nonlinear optimization, and to compare the accuracy of the estimated parameters to the ones obtained using the most accurate linearized form. A third objective was to study the effect of measurement noise level on the accuracy of the Langmuir isotherm. As a result of this study, the following was found. One of the three linearized Langmuir forms provided the most accurate estimates. In fact, its accuracy was even comparable to that obtained by nonlinear optimization using the nonlinear isotherm. In addition, the estimation accuracy was more sensitive to the magnitude of the affinity constant than to the maximum amount of adsorbate in adsorbent; larger values of affinity constant result in higher estimation accuracy of both model parameters. Finally, it was confirmed that the higher the noise content in the variables, the larger the uncertainty of their estimation.

Keywords: Langmuir, Isotherms, Estimation, Sensitivity Analysis, Measurement Noise

1. Introduction

In the past few decades, a great deal of attention has been given to water pollution problems. For example, the removal of toxic heavy metals, such as Zinc, Nickel, and Lead from groundwater and wastewater has been approached by various studies, taking into consideration the serious implications that these pollutants can have on the health of humans and other living organisms. Consequently, many water purification methods have been developed and used to remediate consumable and waste water from those pollutants. These methods include chemical precipitation (Hence, 1998), reverse osmosis (Ning, 2002), electro dialysis, ion exchange, and finally adsorption, which is the focus of this proposal.

Adsorption is a mass transfer process, which involves the contact of solid called adsorbent with a fluid containing certain pollutants called adsorbate (Alkan and Dogan, 2001). These pollutants can be organic compounds, pathogens, and heavy metals, and their contact with the surface of the adsorbent results in permanent bonds, ensuring their removal from the fluid. The adsorption capacity depends on several factors, such as the adsorbent type, its surface area, and its internal porous structure. Additionally, since the attachment of the pollutant can be physical or chemical, the physical and chemical structures as well as the electrical charge of the adsorbent can significantly influence its interactions with the adsorbates, and thus the effectiveness of pollutant removal.

Adsorption processes are characterized by their kinetic and equilibrium isotherms. The adsorption isotherms specify the equilibrium surface concentration of the adsorbate as a function of its bulk concentration. Several mathematical models have been proposed to describe the equilibrium isotherms of adsorption. Some of the most popular models include Langmuir, Freundlich, Redlich-Peterson, and Sips. A summary of these isotherms is provided by Dabaybeh (2001). Even though most of these adsorption isotherms were derived based on some theoretical assumptions about the adsorption mechanism, they involve model parameters that need to be estimated from experimental measurements of the process variables. As an example, the Langmuir isotherm has the following form,

$$q_e = \frac{Q_c b C_e}{1 + b C_e} \tag{1}$$

where, C_e is the equilibrium liquid phase concentration (mg/l), q_e is the equilibrium solid phase concentration (mg/g), Q_c is the maximum amount of adsorbate per unit weight of the adsorbent to form a complete monolayer, and b is a constant related to the affinity between the adsorbent and adsorbate. In the above Langmuir model, Q_c and b are model parameters to be estimated using measurements of the initial and equilibrium concentrations.

Unfortunately, measurements of the adsorption process variables are usually contaminated with noise or measurement errors due to random errors, human errors, or malfunctioning sensors. The presence of such measurement noise, especially in large amounts, can largely degrade the accuracy of the estimated isotherm parameters, which in turn limits the ability of the isotherm to accurately predict the process adsorption capacity. This is because most modeling techniques estimate the model parameters by minimizing some objective functions related to the prediction errors of the model output (q_e). Unfortunately, since the isotherm input and output variables are affected by measurement errors, only minimizing the output prediction errors may not lead to acceptable estimation.

Therefore, the objectives of this project are as follows:

i. Perform a sensitivity analysis to investigate the effect of measurement noise on the estimation accuracy of the Langmuir isotherms for all its linearized forms.

ii. Recommend the best linearized form for Langmuir parameter estimation.

iii. Assess the effect of measurement noise on the parameters estimated from the nonlinear Langmuir model and compare that to the effect on the parameters estimated using the most accurate linearized model.

iv. Assess the effects of different levels of noise on the accuracy of estimated isotherm parameters.

The rest of this paper is organized as follows. In Section 2, a summary of some related recent work is presented, followed by a description of isotherm estimation in Section 3. Then, the effects of measurement noise on the estimation accuracy of the Langmuir linearized forms and the nonlinear form are presented in Section 4, and the results of a sensitivity analysis for the estimation accuracy of model parameters are summarized in section 5. In section 6, the effect of noise content on the estimation accuracy of estimated isotherms is demonstrated for all Langmuir forms. Finally, some concluding remarks are presented in Section 7.

2. Literature Review

Several researchers have addressed the problem of assessing the accuracy of adsorption isotherms. For example, the concept of comparing adsorption isotherms and parameters and evaluating their accuracy by using different models has been discussed by Otun et. al. (2006) for the removal of selected metal ions by powdered egg shell, by Pikaar et. al. (2006) for the sorption of organic compounds to activated carbons, by Ridhika et. al. (2006) for the adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent, and by Karahan et. al (2006) for the removal of boron from aqueous solution by clays and modified clays, and many others. However, these studies focused on determining the best fitting model only for the material, substance or process under study.

Other studies focused on determining the most suitable model to explain the adsorption process depending on the type of instruments used to get the experimental data. For example, Gormi et. Al. (2006) studied the estimation of adsorption-desorption models in the presence of noise in the gas sensors using Langmuir and Wolkenstein. Other studies focused on assessing the effect of some variables on the accuracy of the adsorption parameters. For example, the choice of column hold-up volume, range and density of the data point was found to have an impact on systematic errors in the measurement of adsorption isotherms by frontal analysis (Gritti et. al., 2005). This study showed that the concentration range within which the adsorption data are measured and the way the data points are distributed are important factors in error estimation. In another study of Gritti et. al. (2004), they showed that the fluctuations of the column temperature and the composition and the flow rate of the mobile phase affect the accuracy and precision of the adsorption isotherm parameters measured by dynamic HPLC methods.

Other studies performed statistical analysis on adsorption isotherms to determine the most accurate isotherm, i.e., isotherm model selection. For example, Joshi et. al. (2006) performed model based statistical analysis of adsorption equilibrium data. After comparing the parameter estimation by different linearized and non-linear adsorption models, it was shown that the Langmuir isotherm does not give a satisfying description of the considered experimental data, and that Freundlich isotherm provides the most accurate estimation for the liquid phase concentration range used in the experiment. However, the effect of noise on the accuracy of adsorption parameter estimation has been ignored.

It can be seen that the above studies dealt with analysis or assessment of adsorption isotherms with respect to model selection, effect of certain variables or instruments. In this work, however, the objective is to sturdy the effect of measurement noise on the estimation accuracy of adsorption isotherms. In particular, the focus will be on the Langmuir isotherm to investigate the best method of estimation using a linearized form and the nonlinear form itself.

3. Estimation of Adsorption Isotherms

3.1 Isotherm Model Formulation

Adsorption isotherms are usually nonlinear models relating the adsorption uptake (q_e) to the equilibrium concentration (C_e), which can be expressed as follows:

$$q_e = f\left(C_e, \theta\right) \tag{2}$$

where, θ is a vector of the isotherm parameters to be estimated empirically from experimental measurements. Sometimes, these nonlinear isotherms can be linearized by mathematical manipulations, and can be expressed in a linear form as follows:

$$g_1\left(q_e, C_e\right) = a_1\left(\theta\right) \times g_1\left(q_e, C_e\right) + a_2\left(\theta\right) \tag{3}$$

where, g_1 and g_2 are some functions of the uptake and equilibrium concentration, and a_1 and a_2 are the linearized isotherm parameters, which are functions of the model parameter vector, θ.

Given measurements of the initial concentration and equilibrium concentration data, $\left\{C_o(1) \quad C_o(2) \quad . \quad . \quad C_o(n)\right\}$ and $\left\{C_e(1) \quad C_e(2) \quad . \quad . \quad C_e(n)\right\}$, which are assumed to be contaminated with additive zero-mean Gaussian noise, i.e., $C_o = \tilde{C}_o + \varepsilon_o$ and

$C_e = \tilde{C}_e + \varepsilon_e$ where $\varepsilon_o \sim N(0, \sigma^2)$ and $\varepsilon_e \sim N(0, \sigma^2)$, it is desired to estimate the isotherm parameter vector, θ, that satisfies the relationship:

$$q_e(k) = f(C_e(k), \theta),\ k \in [1, n]. \tag{4}$$

Note that the equilibrium uptake is not measured and in calculated using the initial and equilibrium concentration data follows:

$$q_e = \frac{(C_o - C_e)V}{w} \tag{5}$$

where, V is the volume of the solution and w is the mass of the adsorbent.

The linearized form of equation (4) can be written similar to equation (3) as follows,

$$g_1(q_e(k), C_e(k)) = a_1(\theta) \times g_1(q_e(k), C_e(k)) + a_2(\theta),\ k \in [1, n]. \tag{6}$$

Defining: $g_1(k) \equiv g_1(q_e(k), C_e(k))$, $g_2(k) \equiv g_2(q_e(k), C_e(k))$, $a_1 \equiv a_1(\theta)$, and $a_2 \equiv a_2(\theta)$, equation (6) simplifies to,

$$g_1(k) = a_1 \times g_1(k) + a_2 \tag{7}$$

which can be expressed in matrix form as,

$$\begin{bmatrix} g_1(1) \\ g_1(2) \\ . \\ . \\ g_1(n) \end{bmatrix} = \begin{bmatrix} g_2(1) & 1 \\ g_2(2) & 1 \\ . & 1 \\ . & 1 \\ g_2(n) & 1 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}. \tag{8}$$

Defining: $Y = \begin{bmatrix} g_1(1) \\ g_1(2) \\ . \\ . \\ g_1(n) \end{bmatrix}$, $X = \begin{bmatrix} g_2(1) & 1 \\ g_2(2) & 1 \\ . & 1 \\ . & 1 \\ g_2(n) & 1 \end{bmatrix}$, and $a = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}$, equation (8) reduces to,

$$Y = Xa. \tag{9}$$

3.2 Least Squares Isotherm Estimation

The model parameter vector, θ, can be computed using the estimated linearized isotherm parameters, a_1 and a_2. The linearized model parameters can be estimated using least squares regression by solving the following minimization problem,

$$\{\hat{a}\} = \arg\min_a (Y - Xa)^T (Y - Xa) \tag{10}$$

The above minimization problem has the following closed form solution,

$$\hat{a} = \left(X^T X\right)^{-1} X^T Y \tag{11}$$

Once the parameters a_1 and a_2 are estimated, the isotherm parameter vector θ can be computed using the relations, $a_1 \equiv a_1(\theta)$ and $a_2 \equiv a_2(\theta)$.

3.3 Estimation of Langmuir Isotherm Parameters

Consider the Langmuir isotherm shown in equation (1), where the parameters, Q_c and b, are to be estimated using measurements of C_e. Note that in this case, $\theta = [Q_c \quad b]$.

The Langmuir isotherm can be linearized three different ways as shown below:

$$\frac{1}{q_e} = \left(\frac{1}{Q_c b}\right)\frac{1}{C_e} + \frac{1}{Q_c} \qquad \text{(Langmuir 1)} \qquad (12)$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_c}\right)C_e + \frac{1}{Q_c b} \qquad \text{(Langmuir 2)} \qquad (13)$$

$$\frac{q_e}{C_e} = -b q_e + Q_c b \qquad \text{(Langmuir 3)} \qquad (14)$$

As an example, for the second linearized form (Langmuir 2), $g_1 = \frac{C_e}{q_e}$, $g_2 = C_e$, $a_1 = \left(\frac{1}{Q_c}\right)$, and $a_2 = \frac{1}{Q_c b}$. Therefore, once estimates of the linearized isotherm, $\hat{a}_1$ and $\hat{a}_2$, are obtained using equation (11), estimates of the parameters Q_c and b can be computed as follows,

$$Q_c = \left(\frac{1}{a_1}\right), \text{ and } b = \frac{1}{a_2 Q_c}. \qquad (15)$$

It can be seen from equation (10), that the least squares estimation method relies on minimizing the prediction error of the model output, Y, when estimating the isotherm parameters. This is because it assumes that the input matrix, X, is noise-free. However, there is measurement noise in all variables, and therefore, the matrix, X is also noisy, which violates the basic assumption of this approach. Therefore, the presence of measurement noise in the data can greatly affect the estimation accuracy of estimated isotherms.

4. Effect of Noise on the Estimation Accuracy of the Langmuir Models

4.1 Effect of Noise on the Estimation Accuracy of the Linearized Langmuir Models

Since there are three different linearized forms for the Langmuir isotherms, it is expected to get three different estimates of the isotherm parameters. This is because the three forms minimize different objectives functions in the estimation of the isotherm parameters. Therefore, in this section, the objective is to study the effect of measurement noise on the estimation accuracy of the three linearized Langmuir forms, which will lead to the selection of the best form for estimating the isotherm parameters.

To perform this study, the Langmuir isotherm is used to generate data assuming Q_c =150, and b=0.15. These data are assumed to be noise-free. Then, the initial and equilibrium concentration data are contaminated with zero mean Gaussian noise of variance 0.5. Then, the noisy data are used to estimate the isotherm parameters using the three linearized forms as described in Section 3. To provide a statically meaningful results, a Monte Carlo simulation of 1000 realizations is performed, and the distributions of the estimated parameters are constructed for the three linearized forms as shown in Figures 1 and 2 for the parameters, Q_c and b, respectively.

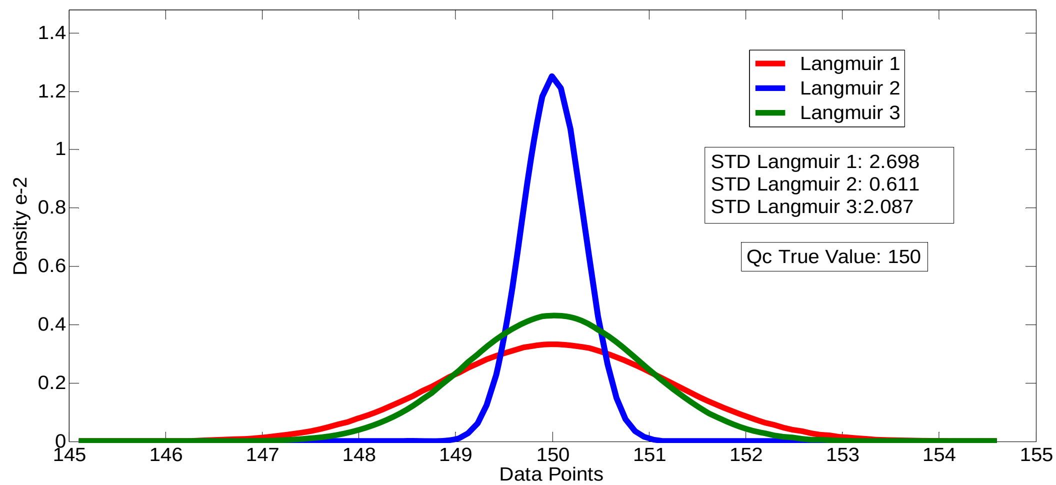

Figure 1. Comparison of the accuracy of estimated *Qc* using the three linearized Langmuir forms

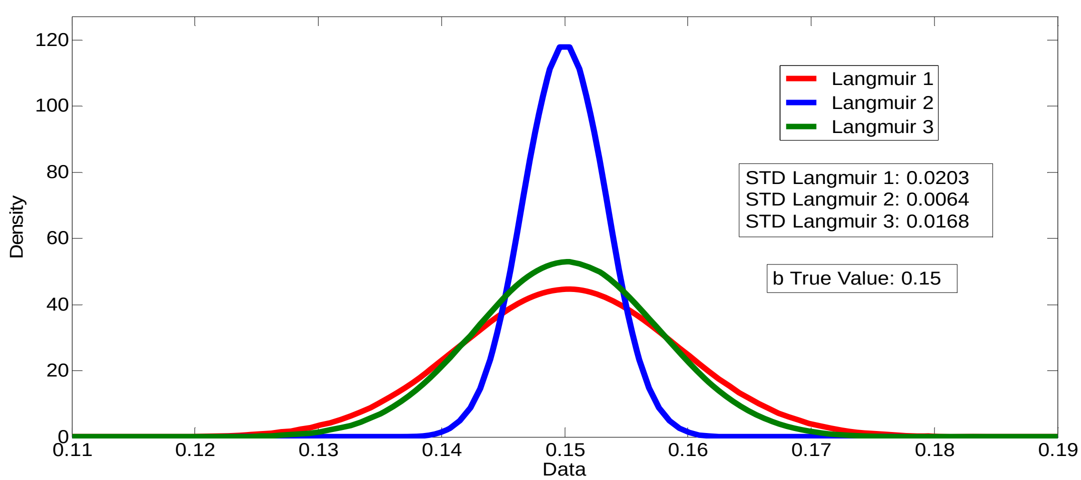

Figure 2. Comparison of the accuracy of estimated *b* using the three linearized Langmuir forms

Both Figures 1 and 2 show that the second linearized form of Langmuir provides the best estimated of the model parameters. This is also demonstrated by the standard deviations of the estimated parameters by the three forms as shown in Table 1.

Table 1. Standard deviations of the estimated parameters for the three linearized Langmuir forms

	Qc	*b*
Langmuir 1	2.698	0.0203
Langmuir 2	0.611	0.0064
Langmuir 3	2.087	0.0168

Therefore, the second linearized form of Langmuir, shown in equation 13, provides the most accurate estimates for the adsorption parameters.

4.2 Effect of Noise on the Estimation Accuracy of the Nonlinear Langmuir Model

In this section, the estimation accuracy of the best linearized form of the Langmuir isotherm (Langmuir 2) is compared to that based on the nonlinear model itself. The parameter estimates based on the nonlinear model are obtained using nonlinear optimization as follows:

i. A mesh of the possible *Qc*- *b* values is created as shown in Figure 3.
ii. At each node (i.e., {*Qc*,*b*} pair), the values of the equilibrium uptake, q_e, is computed given the values of the equilibrium concentrations, C_e.
iii. The mean squares errors between the predicted q_e and the measured values are computed at each node.
iv. The isotherm parameter pair {*Qc*,*b*} that provides the minimum mean squares error is selected as the optimum isotherm parameters.

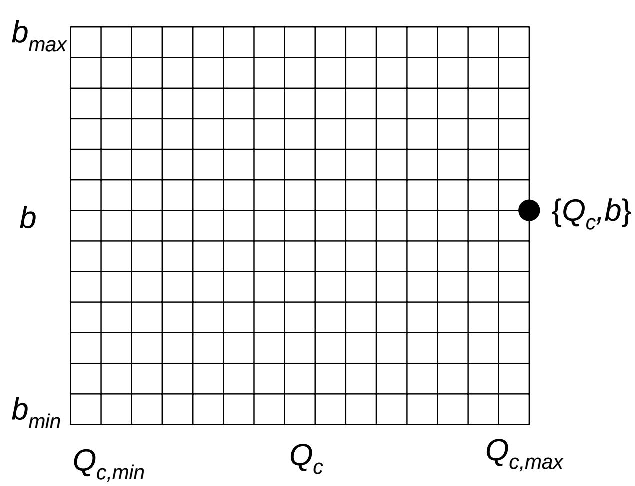

Figure 3. The mesh used to estimate the optimum {*Qc*,*b*} pair based on the nonlinear Langmuir isotherm

To compare the accuracy of estimated isotherm parameters using Langmuir-2 and the nonlinear model, a Monte Carlo simulation is performed similar to the one described in Section 4.1, but for both the linearized and nonlinear forms and for different values of *Qc* and *b*, and the results are illustrated in Figures 4 and 5. Figures 4 and 5 show that the accuracies obtained using the second linearized isotherm form (Langmuir-2) and the nonlinear model, are comparable and differ for different magnitudes of *Qc* and *b*. For example, for small values of *b*, the nonlinear model provided slightly better estimates of the parameters, but for larger values of *b*, the linearized model provided better results.

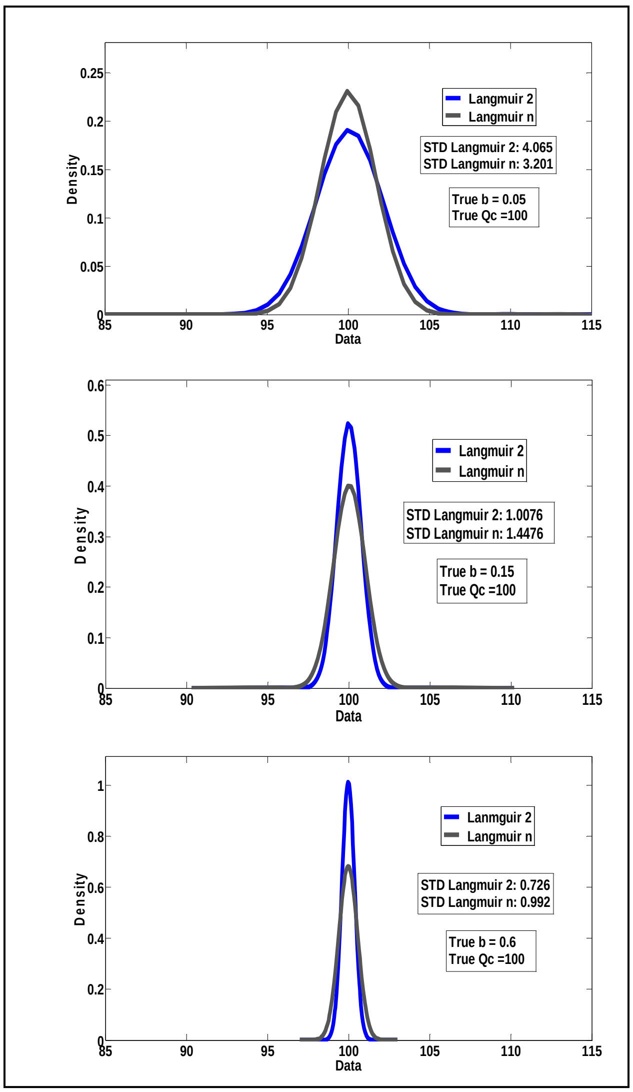

Figure 4. *Qc* estimation by Langmuir n and Langmuir 2 as b decreases

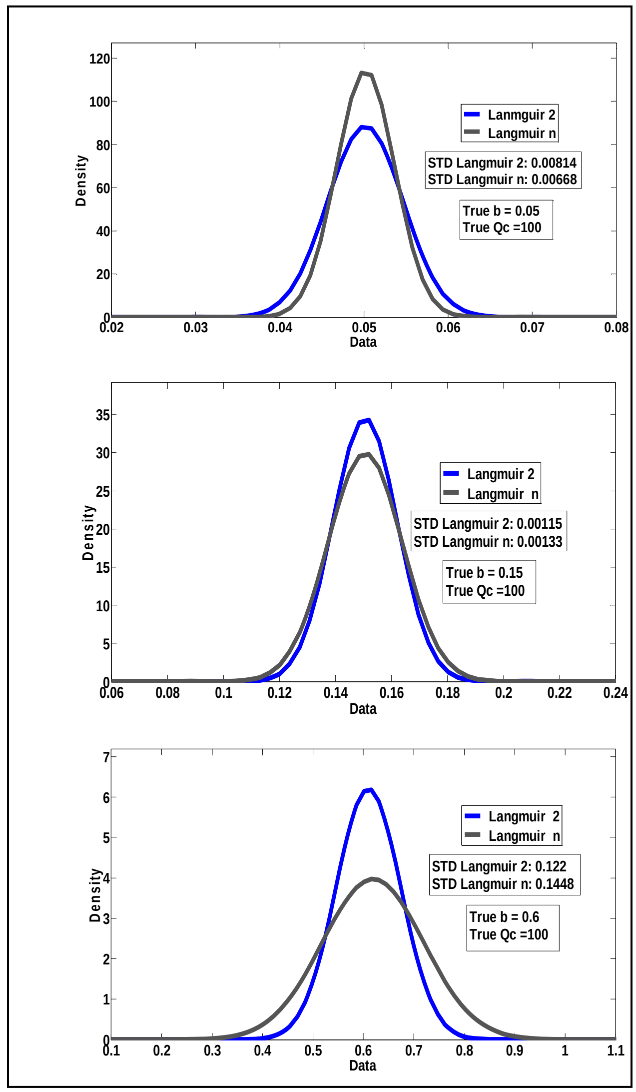

Figure 5. *b* estimation by Langmuir n and Langmuir 2 as b decreases

5. Sensitivity Analysis for the Estimation Accuracy of Model Parameters *Qc* and *b*

5.1 Estimation of *Qc* and *b* in Linearized Langmuir Models

The variation of *Qc* true value, at fixed *b* values, shows no significant effect on the distribution of *Qc* experimental data obtained from the three linearized models. On the other hand, increasing the true value of *b*, at *Qc* fixed values, shows that the standard deviation of data distribution for the three models decreases and the three models gives better and closer estimation. Also, the data fit according to Langmuir 3 and Langmuir 1 becomes increasingly more similar. In fact, the effect of *b* variation is most significant on Langmuir 1 estimation whose standard deviation changes significantly with the change in b value. Finally, increasing the true values of both parameters *Qc* and *b*, simultaneously, shows that the effect of the variation of *b* dominate the way the models' estimation for parameters changes; i.e. the results are very similar to those obtained in the case of *b* variation. A summary of the aforementioned results is demonstrated in Appendix A.

Equally true, the results of varying the parameters' magnitude on *b* estimation by the three linearized Langmuir models are the same as those on *Qc* estimation. A summary of those results is illustrated in Appendix B.

5.2 Estimation of *Qc* and *b* in Nonlinear Langmuir Model

Similar to the results of the linearized forms, the variation of *Qc* true value, at fixed *b* values, shows no significant effect is noticed on the distribution of *Qc* experimental data obtained from the two models. On the other hand, under very small *b* values, the nonlinear model Langmuir n gives better estimation for *Qc* parameter than the linear model Langmuir 2. As *b* increases, however, Langmuir 2 estimation improves and becomes more accurate than that of Langmuir n. Also, as *b* true value increases, it is noticed that the standard deviation of data distribution for the two models decreases and thus both models give better and closer estimation. Finally, increasing the true values of both parameters *Qc* and *b*, simultaneously, shows that the effect of the variation of *b* dominate the way the models' estimation for parameters changes; i.e. the results are very similar to those obtained in the case of *b* variation. A summary of the aforementioned results is demonstrated in Appendix C.

Again, the results of varying the parameters' magnitude on *b* estimation by the nonlinear Langmuir model are the same as those on *Qc* estimation. A summary of those results is illustrated in Appendix D.

6. Effect of Noise Content on the Estimation Accuracy of Estimated Isotherms

In this study, the effect of noise content in the measured variables on the estimation accuracy of the Langmuir isotherm parameters is investigated. To do that, the sensitivity analysis performed in Sections 4.1 and 4.2 are repeated for different noise levels (variances of 0.1, 0.5, and 0.9), and the results are illustrated in Figures 6 and 7. In these Figures, the line colors denote the following: red: Langmuir-1, blue: Langmur-2, green: Langmuir-3, grey: nonlinear model. As expected, these Figures show that for larger noise contents (higher noise variance), the uncertainty of the estimated parameters increases.

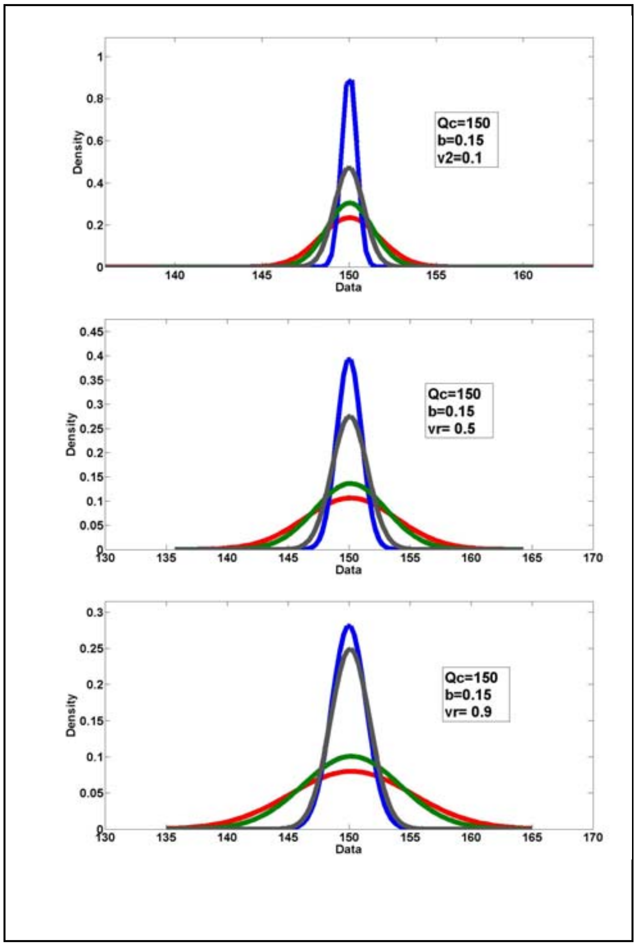

Figure 6: The effect of noise variation on the estimation of *Qc*

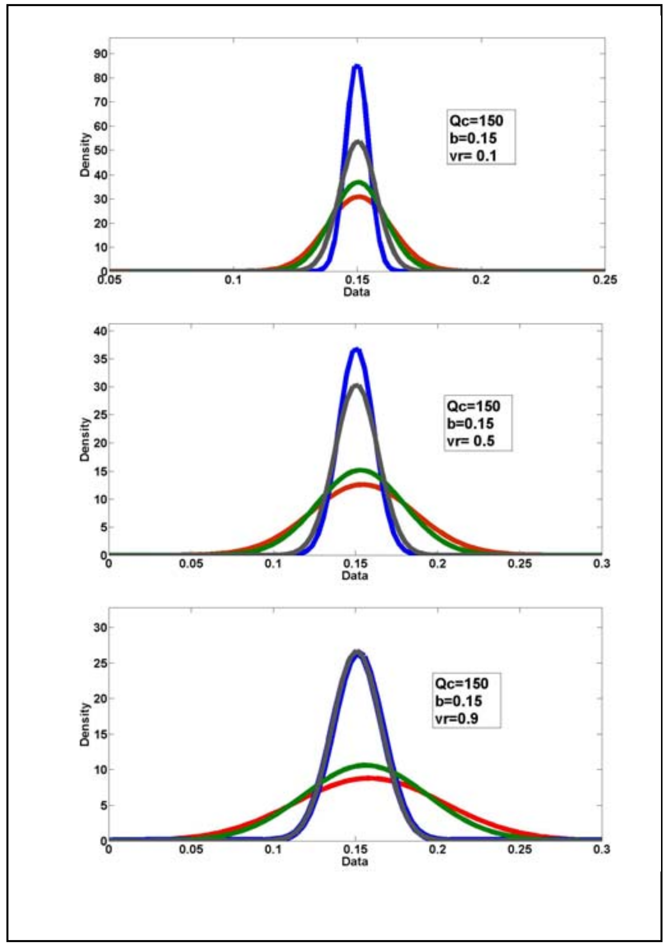

Figure 7: The effect of noise variation on the estimation of *b*

7. Conclusions

In this project, a statistical analysis of the Langmuir isotherm was preformed. It was found that out of three linearized isotherms forms of Langmuir, (Langmuir-2) provides the most accurate estimates of the isotherm parameters. In fact, Langmuir-2 provides comparable estimated to the ones obtained using the nonlinear isotherm form. This is an important finding because it is more computationally expensive to estimate the isotherm parameters by nonlinear optimization. It is also confirmed that the level of noise in the adsorption data degrades the estimation accuracy of estimated isotherm parameters.

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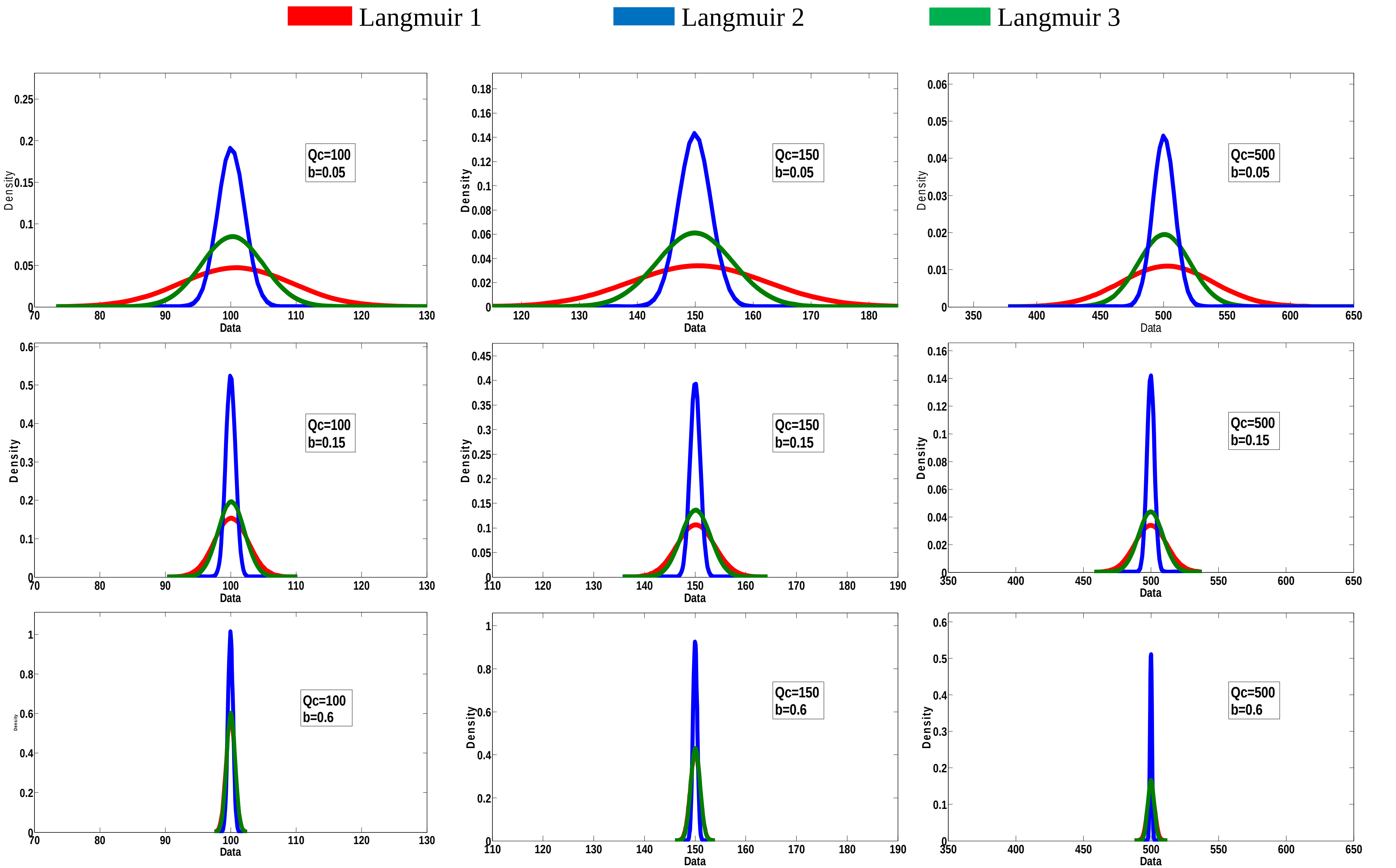
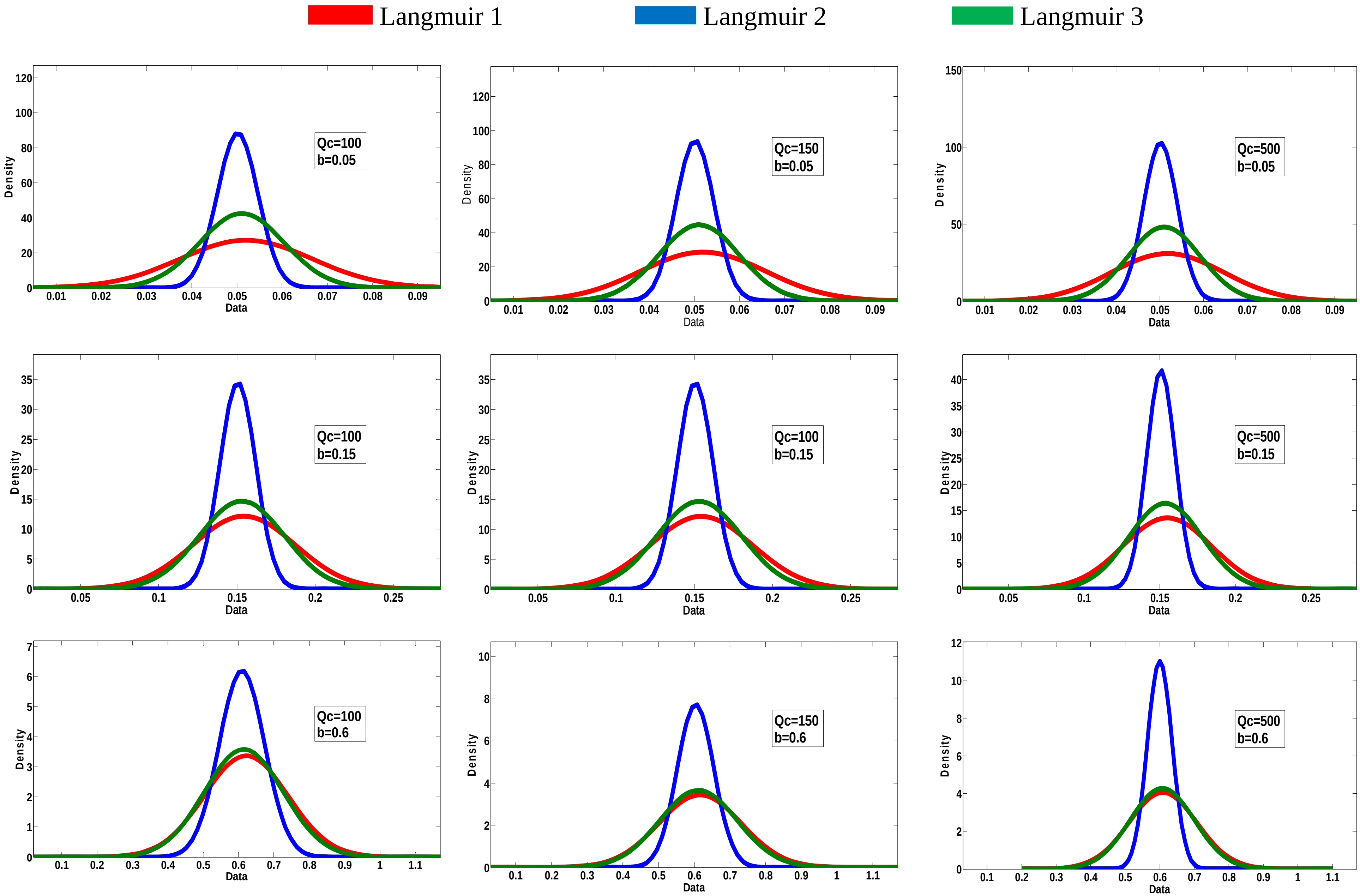
Appendix A

The variation of *Qc* estimation by the linearized Langmuir models as function of *Qc* and *b* true values



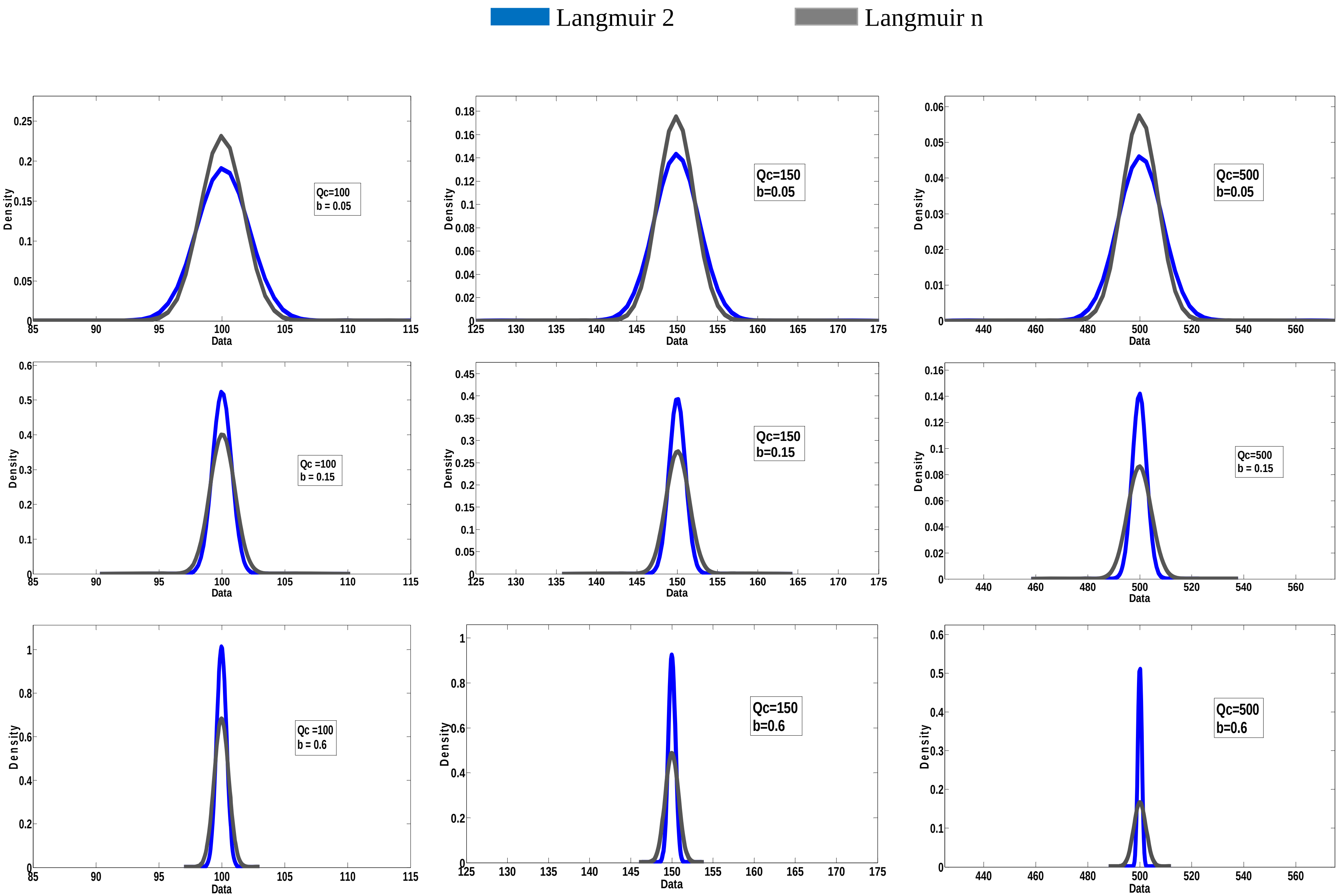
Appendix B

The variation of *b* estimation by the linearized Langmuir models as function of *Qc* and *b* true values



Appendix C

The variation of *Qc* estimation by Langmuir 2 and Langmuir n as function of *Qc* and *b* true values



Appendix D

The variation of *b* estimation by Langmuir 2 and Langmuir n as function of *Qc* and *b* true values