SENSITIVITY ANALYSIS OF ADSORPTION ISOTHERMS SUBJECT TO MEASUREMENT NOISE IN DATA

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ABSTRACT

Reflecting the importance of adsorption as a major water purification method, the main objective of this research was to perform a sensitivity analysis on some of the common adsorption isotherms subject to measurement noise in data. Even though most of adsorption isotherms have been derived based on theoretical assumptions about the adsorption mechanism, they involve model parameters that need to be estimated from experimental measurements of the process variables. Specifically, for the Langmuir isotherm, which can be linearized in three forms, it was sought to determine which of these three forms would give the highest accuracy of the adsorption model parameters – maximum amount of adsorbate per unit weight of the adsorbent and the constant related to the affinity between the adsorbent and adsorbate. Another objective was to estimate the adsorption parameters using the nonlinear Langmuir model, and to compare their accuracy to the ones estimated using the most accurate linear form. Furthermore, it was desired to examine the effect of noise magnitude on the estimation accuracy for the various Langmuir forms (linear or nonlinear) by varying the noise variance and the magnitude of the adsorption parameters themselves. To achieve this aim, MATLAB programming software was used for simulations. The results of this work could be summarized as follows: One of the linearized forms of Langmuir model showed normal distribution and provided most accurate estimation of both model parameters. In addition, it was shown that when the noise content (standard deviation) increased on the data, less accurate estimates were obtained for both adsorption parameters. Finally, 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.

Keywords: Langmuir, linearization, parameters, noise

INTRODUCTION

During the last few decades and as industries were growing, significant pollution problems rose up, and handling them became a major concern especially for scientists and engineers. In specific, a great deal of attention has been given to water pollution problems as they threat one of the most vital natural resources for human life. For example, the removal of toxic heavy metals (such as Zinc, Nickel, and Lead) from groundwater and wastewater has been approached by various works and studies, taking into consideration the very serious implications that these pollutants can have on humans' and other living beings' health. Consequently, many water purification methods has been developed and used to remediate consumable and waste water from those pollutants. These methods include chemical precipitation (Hence [1]), reverse osmosis (Ning [2]), electro dialysis, ion exchange, and finally adsorption.

In general, 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 [3]). 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 [4]. 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. Talking about Langmuir model in specific, the 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 from measurements of q_e and C_e.

Unfortunately, measurements of the adsorption process variables, q_e and C_e, 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 adsorption capacity of a certain process. This is because most modeling techniques estimate the model parameters by minimizing some objective function related to the prediction errors of the model output (q_e). Unfortunately, since the isotherm input and output variables (q_e and C_e) are both measured, only minimizing the output prediction errors may not lead to acceptable estimation.

Therefore, the objectives of this project were as follows:

1. Perform a sensitivity analysis to investigate the effect of the presence of measurement noise on the estimation accuracy of the Langmuir model isotherms (linear and non-linear). The effect of noise on the estimated parameters from each of these linearized models was assessed, and recommendations on the best linearized model were provided. Of course, the sensitivity analysis results will also depend on the estimation method utilized.

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

3. Assess and compare the effects of different noise intensities and parameters (*Qc* and *b*) magnitude on the latter's accuracy estimation.

LITERATURE REVIEW

Being a major mass transfer process of multiple uses, researches continue about adsorption process, its mechanisms, and its application in various fields. As it has been noted, the basic concern of this study is to perform a general sensitivity analysis for adsorption isotherms, using artificially added noise, to detect the best form of Langmuir model for adsorption parameters' estimation. In this regard, this study intersects with some of the researches done before in the same field, while being unique.

For example, the concept of comparing adsorption isotherms and parameters and evaluating their accuracy by using different models has been discussed for: the removal of selected metal ions by powdered egg shell (Otun et al. [5]), sorption of organic compounds to activated carbons (Pikaar et al. [6]), adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent (Radhika and Palanivelu [7]), removal of boron from aqueous solution by clays and modified clays (Karahan et al. [8]), and many others. However, it is clear that these studies determine the best fitting model only for the material, substance or process under study. Similarly, some studies determined the most suitable model to explain the adsorption process depending on specific type of instrument used to get the experimental data; Modeling in Adsorption-Desorption Noise in Gas Sensors Using Langmuir and Wolkenstein for Adsorption (Gormi et al. [9]) forms a good example. In this regard, the current project provides more general information about the most accurate Langmuir model, regardless of the substance tested or the instrument used.

On the other hand, some researches focused on studying the effect of some variables on the accuracy of the adsorption parameters' estimation by various models. 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 and Guiochon [10]). This study shows 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. Another study for Gritti and Guiochon [11] shows 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". Yet, this study base its findings on experimental data (acquired by frontal analysis FA), and is applied on specific system (phenol in equilibrium between C18-bonded Symmetry and a methanol-water mixture).

In addition, it was noticed that some studies performed statistical analysis on adsorption isotherms to determine the most accurate model in estimating the adsorption parameters. For example, Joshi et al. [12] 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 "Langmuir model 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, again, the effect of noise (found in the experimental data due to human or instrumental error) on the accuracy of adsorption parameter estimation has been ignored. This effect is highlighted in the current paper by adding artificial noise to noise free data and then detecting the change in the parameters' value by different Langmuir models. In addition, while the estimation accuracy in the latter paper is compared between different models, our current paper aims to compare between the accuracy of non-linear Langmuir model and that of its possible linearized forms.

EXPERIMENTAL PROCEDURE

To start with, the simulation of this study was performed using MATLAB programming software.

Part One: Linearized Langmuir Models

The Langmuir could be linearized in three forms:

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

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_c}\right)C_e + \frac{1}{Q_c b} \qquad \text{Langmuir 2} \qquad (3)$$

$$\frac{q_e}{C_e} = -b\, q_e + Q_c b \qquad \text{Langmuir 3} \qquad (4)$$

The above linearized models would provide different parameter estimation results as they minimize different objective functions. After simulating each of these models on MATLAB, noise-free inputs and outputs (q_e and C_e) were used based on already given *Qc* and *b* values. Then, noise was added to the noise-free data (q_e and C_e), and *Qc* and *b* of each linearized model were estimated to quantify the impact of measurement noise on the accuracy of their estimation. Having randomly distributed noise, the simulation was repeated 1000 times to get 1000 different estimated values for *Qc* and *b* in every run. Then, the different estimates for every parameter were statistically analyzed to show their distribution pattern and deviation from the true value.

Part Two: Non-linear Langmuir Model

To simulate the nonlinear model on MATLAB, genetic optimization algorithm – which is widely used in nonlinear optimization – was used. In details, the objective function of the prediction error was evaluated over a mesh of the model parameters, and then a minimum was selected over the entire mesh. Similar to the linearized models, the simulation was repeated 1000 times to get 1000 different estimated values for *Qc* and *b* in every run. Then, the different estimates for every parameter were statistically analyzed to show their distribution pattern and deviation from the true value, and they were plotted together with the estimated parameters of the linearized models for accuracy comparison.

Part Three: Noise Intensity and Parameters Magnitude Effects

Each of the procedures explained above was repeated with three different variances (noise magnitude). In addition, the simulations were carried using various combinations of three different (progressively increasing) values of *Qc* and *b*.

RESULTS AND DISCUSSION

Best Linearized Langmuir Model

Qc and *b* estimates distribution pattern for the three linearized models is represented in Figures 1 and 2, respectively. Figure 1 shows that the *Qc* distribution pattern for

Langmuir 2 is closer to the true value than that of Langmuir 3 whose distribution pattern is in turn closer than that of Langmuir 1. This was proven by the standard deviation values for the three models: The standard deviation of *Qc* from its true value for Langmuir 1 is 0.611, smaller than that of Langmuir 3 (2.087) which is in turn smaller than that of Langmuir 1 (2.698). Similar results are demonstrated in figure 2 where the standard deviation of *b* from its true value for Langmuir 2 is 0.0064, smaller than that of Langmuir 3 (0.0168) which is in turn smaller than that of Langmuir 1 (0.0203). These results were confirmed by testing different true values of *Qc* and *b* and under variable noise intensity (as will be shown). As a result, Langmuir 2 linearized form proves to provide the most accurate estimating for the adsorption parameters upon applying experimental noise.

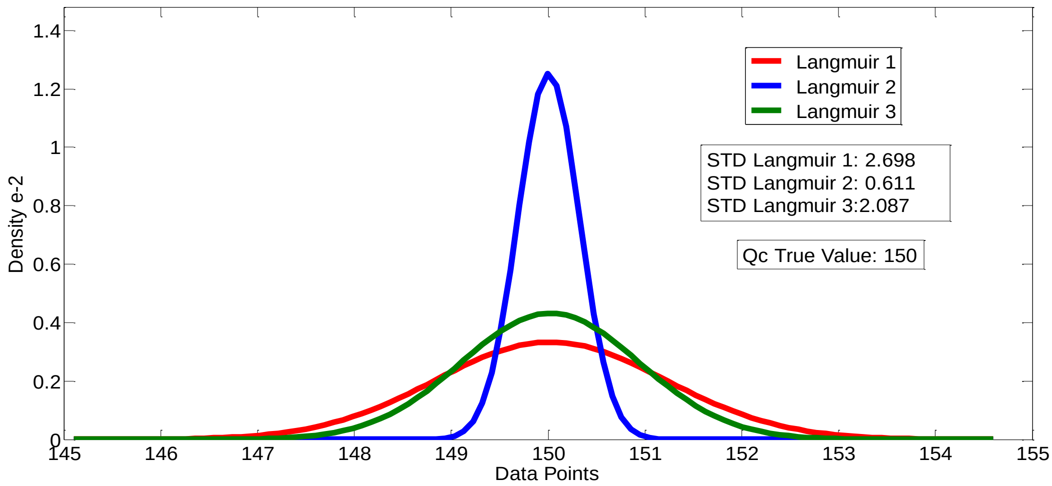

Figure 1: *Qc* Estimation Using the Three Linear Langmuir Model

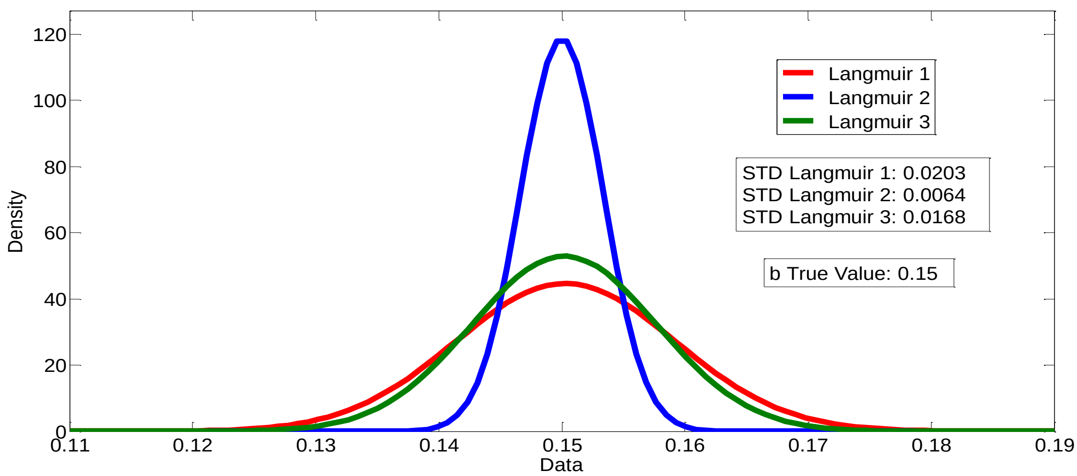

Figure 2: *b* Estimation Using the Three Linear Langmuir Models

Nonlinear Langmuir Model

Qc and *b* for both the nonlinear and Langmuir 2 models were plot as shown in Figures 3 and 4, respectively. Figure 3 shows that while the nonlinear model gave better estimation for *Qc* than Langmuir 2 at very small *b*, Langmuir 2 proved superior as *b* value increased. Those results were confirmed by the standard deviation for *Qc* values of both models as *b* increases: when b is relatively very small, the standard deviation of *Qc* from its true value by Langmuir n was 3.201, smaller than that given by Langmuir 2 (4.065). However, as *b* increases to 0.15 and beyond, the standard deviation of *Qc* by Langmuir 2 become smaller than that by Langmuir n. The same results were shown for b estimation by the two models in Figure 4.

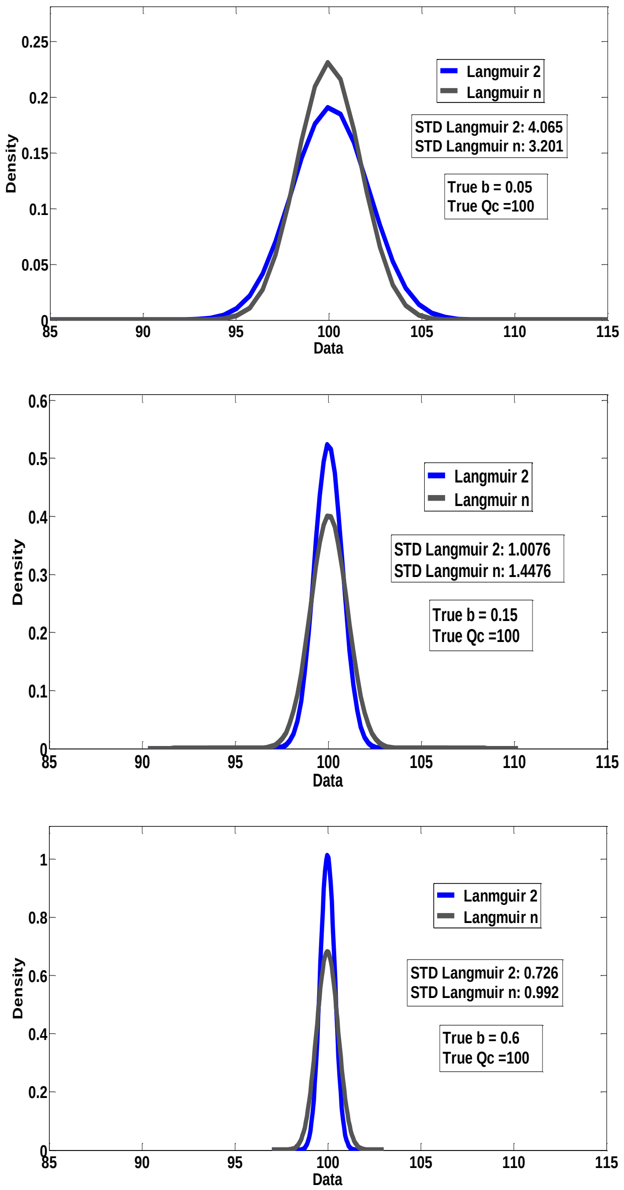

Figure 3: Qc estimation by Langmuir n and Langmuir 1 as b decreases

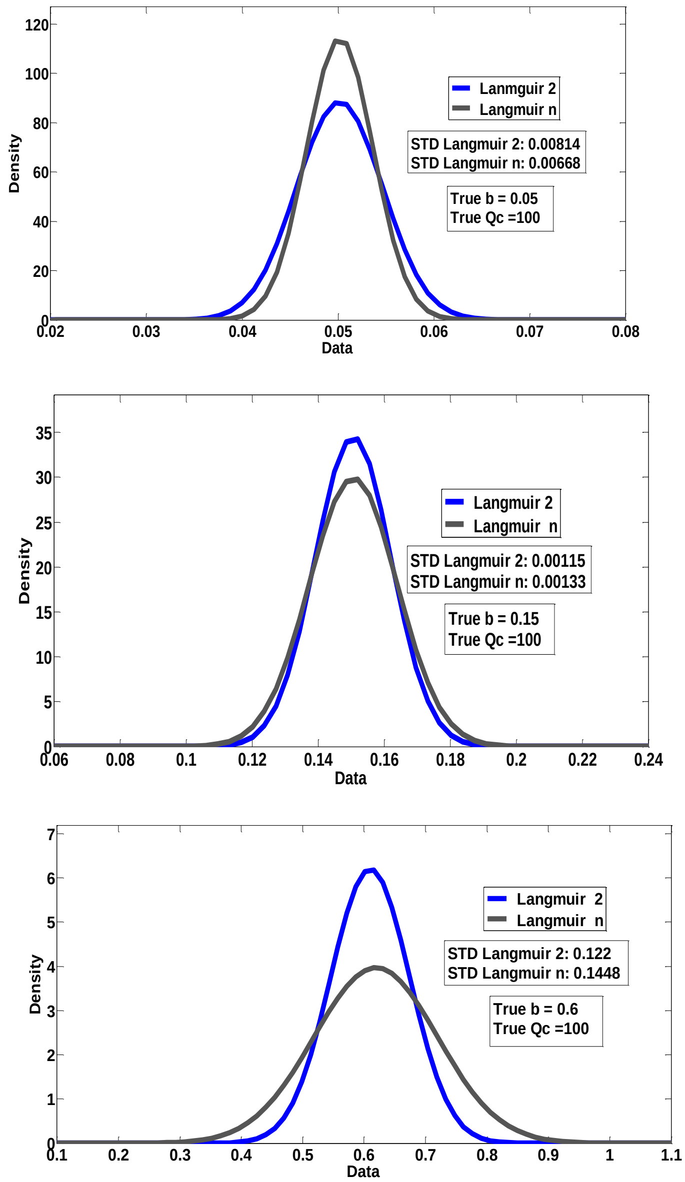

Figure 4: b estimation by Langmuir n and Langmuir 1 as b decreases

Comparison of Langmuir Linearized Form

Variation of Parameters: Effect on *Qc* Estimation

The results of variation of parameters' magnitudes on *Qc* estimation by three Langmuir models are clearly demonstrated in Appendix A.

- Upon the variation of *Qc* true value (*b* remains constant), no significant effect is noticed on the distribution of *Qc* experimental data obtained from the three Langmuir models.
- When b true value increases (*Qc* remains constant), it is noticed 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. On the other hand, as *b* true value decreases, it is noticed that the standard deviation of data distribution for the three models increases, the three models gives worse and broader estimation, and distribution patterns provided by Langmuir 1 and Langmuir 3 become more and more different. Finally, the effect of *b* variation is most significant on Langmuir 1 estimation whose standard deviation changes significantly with the change in b value.
- When both *Qc* and b increases, the effect of the variation of *b* remains significant and dominate the way the models' estimation for parameters changes; i.e. the results are very similar to those obtained incase of *b* variation.

Variation of Parameters: Effect on *b* Estimation

The results of the variation of parameters' magnitudes on *b* estimation by three Langmuir models are clearly demonstrated in Appendix B.

- The effects of parameters' magnitude on *b* estimation by the three Langmuir models are the same as those on *Qc* estimation. Yet, it is worth mentioning that those effects are more significant for *Qc* than for b estimation, under the same conditions.

Comparison of Nonlinear and Most Accurate Linear Forms

Variation of Parameters: Effect on *Qc* Estimation

The results of variation of parameters' magnitudes on *Qc* estimation by Langmuir 2 Langmuir n are clearly demonstrated in Appendix C.

- Upon the variation of *Qc* true value (*b* remains constant), no significant effect is noticed on the distribution of *Qc* experimental data obtained from the two models.
- 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 even better 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.

- When both *Qc* and b increases, the effect of the variation of *b* remains significant and dominate the way the models' estimation for parameters changes; i.e. the results are very similar to those obtained incase of *b* variation.

Variation of Parameters: Effect on *b* Estimation

The results of variation of parameters' magnitudes on *b* estimation by Langmuir 2 Langmuir n are clearly demonstrated in Appendix D.

- Unlike all other cases, as *Qc* true value increases (*b* remains constant), the estimation of *b* by both linear and nonlinear models slightly improves.

- Under very small *b* values, the nonlinear model Langmuir n gives better estimation for *b* parameter than the linear model Langmuir 2. As *b* true value increases, its estimation by Langmuir 2 improves and becomes even better 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. Yet, it is worth mentioning that the latter effect is more significant for *Qc* than for b estimation, under the same conditions.

- When both *Qc* and b increases, the effect of the variation of *b* remains significant and dominate the way the models' estimation for parameters changes; i.e. the results are very similar to those obtained incase of *b* variation.

Noise Variation Effect

The effect of noise variation on both *Qc* and *b* estimation is demonstrated clearly in Figures 5 and 6, respectively.

- As it was expected, when the level of noise added to the true data increases, the standard deviation of both *Qc* and *b* data distribution by the linear and nonlinear models increases. This signifies that these models give broader and less accurate estimation.

- At very low levels of noise the nonlinear Langmuir model becomes increasingly similar to that of Langmuir 2. Yet, as the variance of noise increases, the nonlinear model estimation for *Qc* and *b* deteriorates significantly and Langmuir 2 retains providing the most accurate estimation for the adsorption isotherms' parameters.

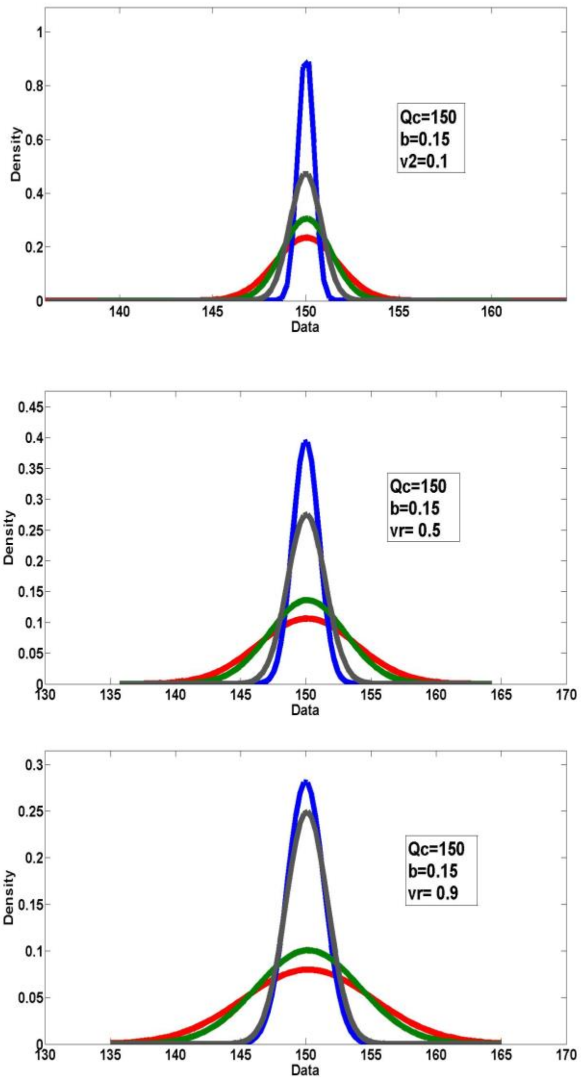

Figure 5: Effect of noise variation on *Qc* estimation

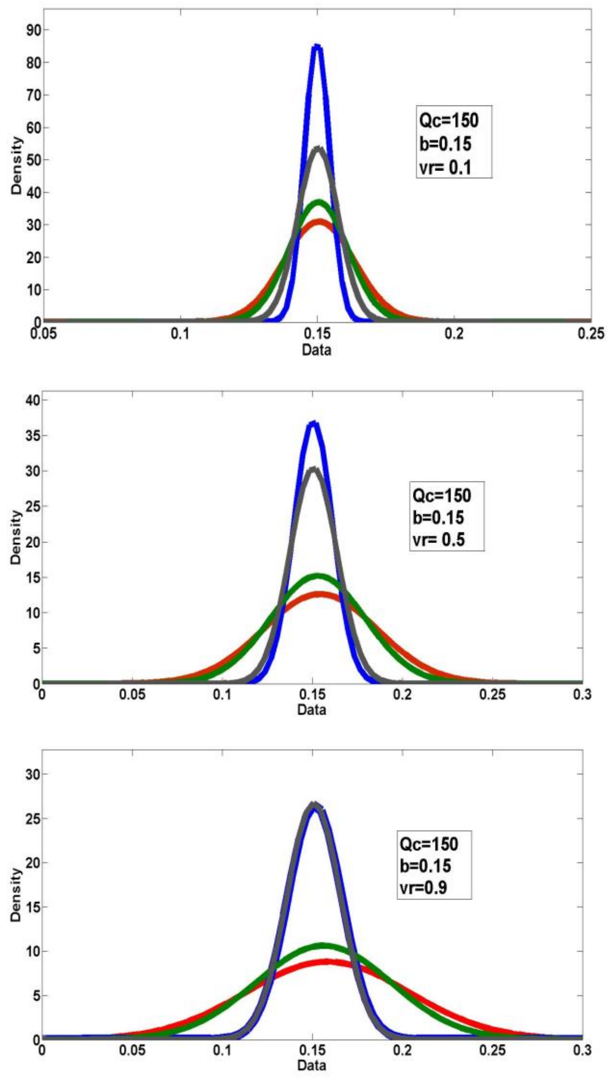

Figure 6: effect of noise estimation on *b* estimation

CONCLUSIONS AND RECOMMENDATIONS

From the previous analysis for the Langmuir models it could be concluded that:

- Langmuir 2 is the most accurate linearized form of Langmuir model to estimate the adsorption parameters *Qc* and *b.*

- Langmuir n and Langmuir 2 give very close estimates for the adsorption parameters.

- *Qc* value has no significant effect on the adsorption parameters' estimation.

- As the affinity constant between the adsorbent and adsorbate magnitude increases: the estimation of *Qc* and *b* by all models improves and Langmuir 2 proves superior.

These results allow better understanding of the adsorption modeling by Langmuir. Thus, depending on the experimental conditions specified, it would be easier to determine which Langmuir form would give them most accurate adsorption parameters and thus the most accurate modeling. In addition, the results prove to be of significant practical value. From on side, now that it is known that the second linearized form gives at least the accuracy than the original model, this linearized form can be used with high level of confidence to get accurate estimations for the final equilibrium solid phase concentration q_e. On the other hand, the suggested Langmuir 2 provides a more accurate alternative for the linearizing the Langmuir model than Langmuir 1 used by most industries.

Finally, after determining the best linear Langmuir model, comparing this model with the original nonlinear form, and determining the effect of noise and parameters' magnitude on the latter's estimation accuracy, it is highly recommended to carry similar analysis on other adsorption models (Freundlich, Redlich-Peterson, Sips…etc) and compare their respective estimation accuracy with that of Langmuir n and Langmuir 2. This would allow having a thorough knowledge about the parameters' estimation accuracy of various adsorption models. Eventually, it would permit better adsorption modeling and thus more accurate results in the various practical fields of adsorption, especially water pollution.

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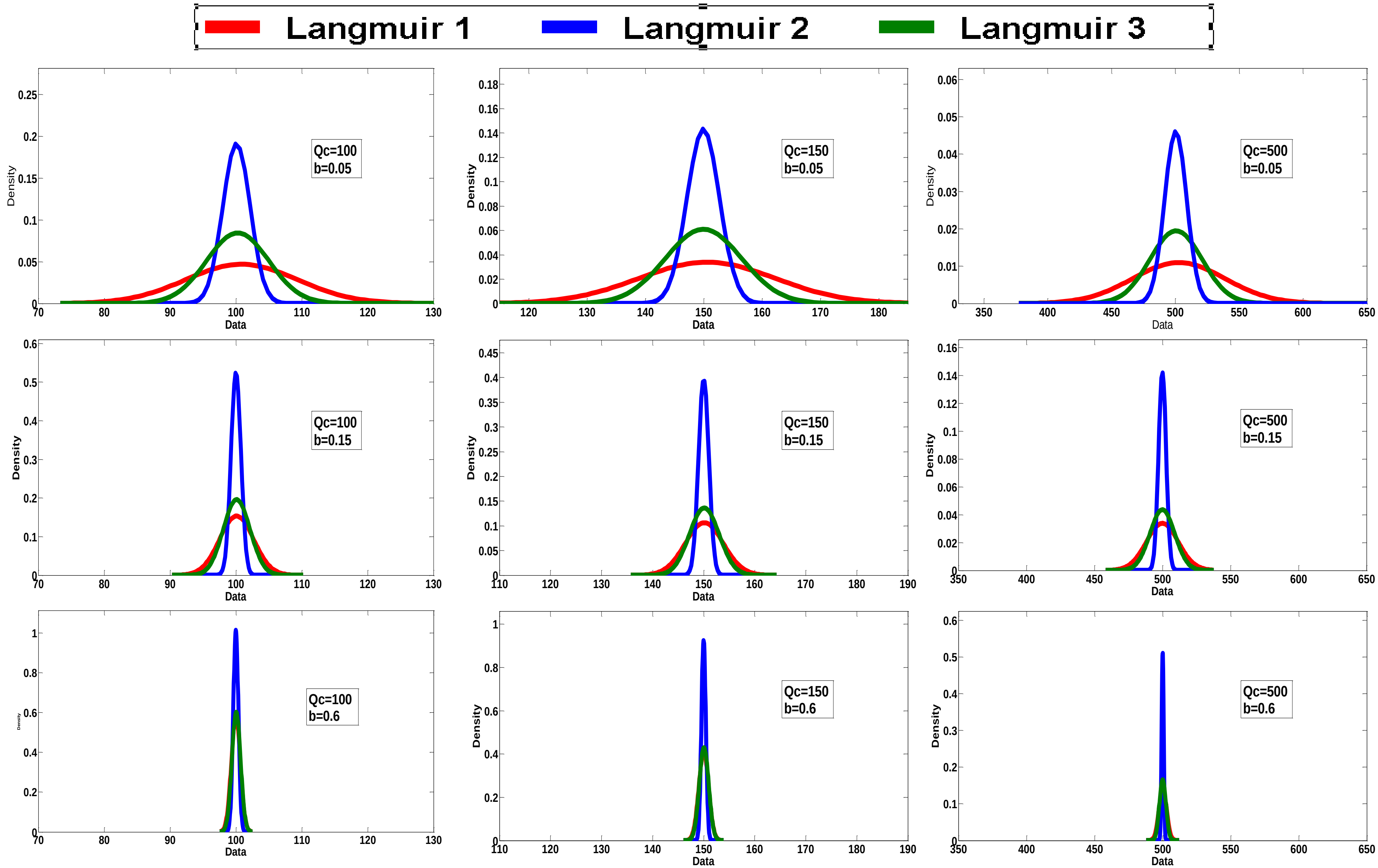
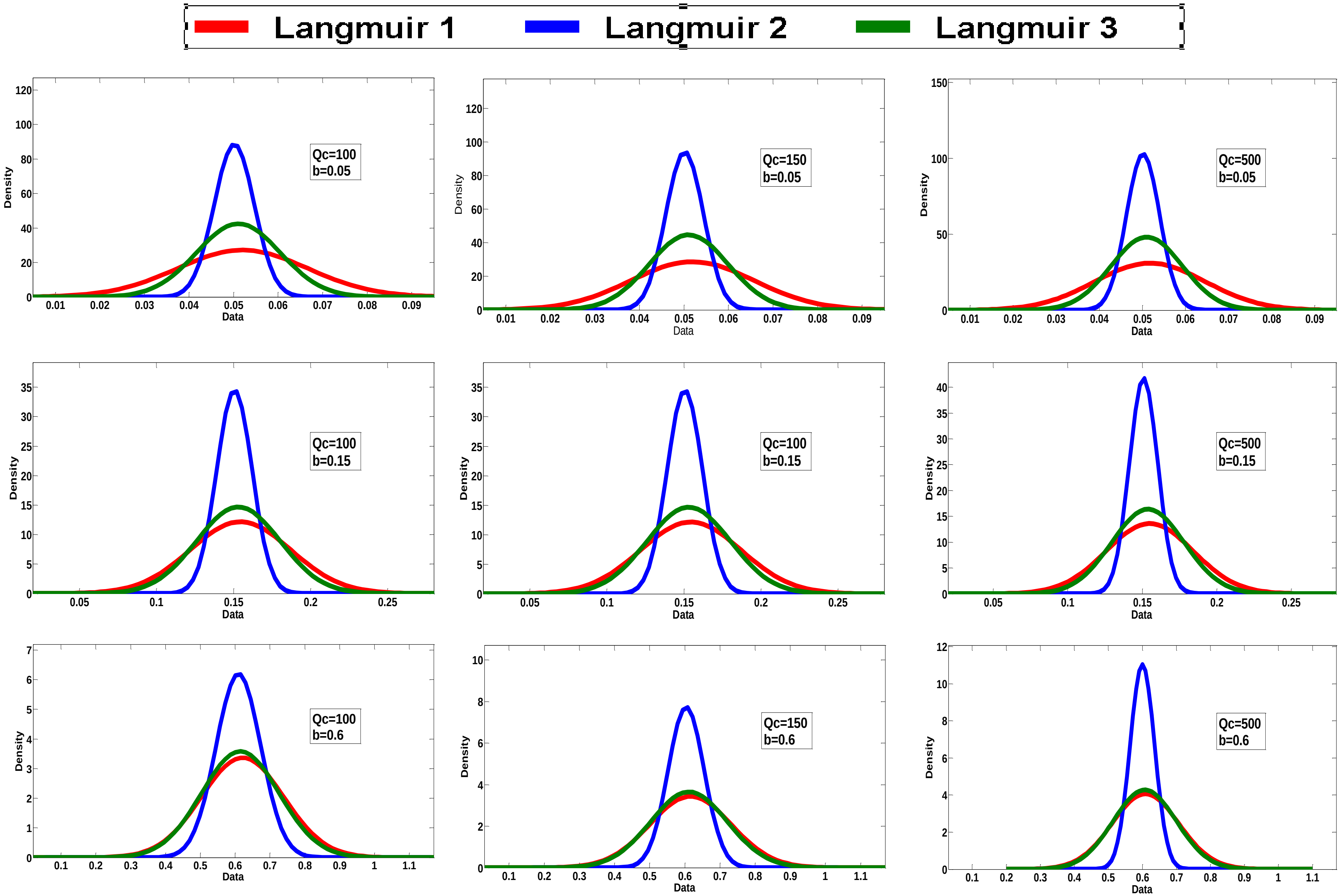
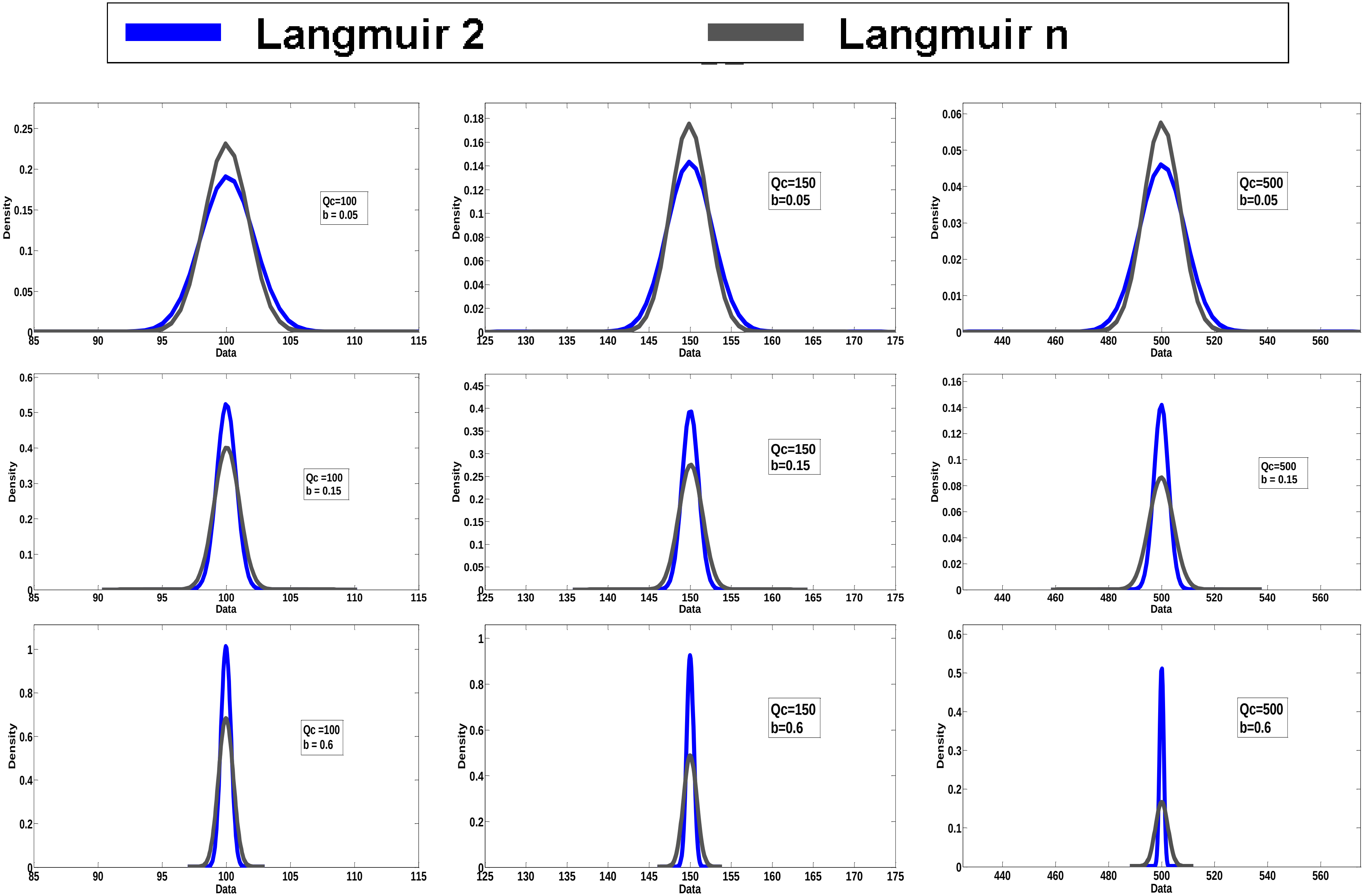
Appendix A: The variation of *Qc* estimation by the linearized Langmuir models as function of *Qc* and *b* true values



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