

**Statistical analysis of adsorption experimental data  
– the influence of the selection of error function  
on optimized isotherm parameters**

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Experimental adsorption data were analysed by fitting them to nonlinear forms of Langmuir and Freundlich isotherms. Optimization of the parameters was performed by nonlinear least square regression with different forms of error function, namely: vertical, horizontal, orthogonal, normal and squared normal. The results showed, that isotherm parameters may be affected by the selection of error function and that they are more sensitive to its' form in case of Langmuir equation. We did not find any correlation between a type of the function and performance of the regression – procedure requires optimization for every experimental dataset and every model being fitted.

## 1. INTRODUCTION

One of the processes that is most commonly applied in the industry, *e.g.* a wastewater treatment, is adsorption [1-4]. Hence, much effort is put into quantitative and qualitative description of this process. One of the models that is most widely used is a Langmuir model [5], which can be denoted in a form of the following isotherm:

$$a = a_m \frac{Kc}{1 + Kc} \quad (1)$$

where  $a$  stands for adsorbed amount,  $a_m$  monolayer capacity,  $K$  and  $c$  for adsorption constant and equilibrium concentration of the adsorbate, respectively. This model has strong theoretical foundations – it assumes that adsorption is localised, surface is energetically homogenous and there is no interaction between adsorbed particles. The constant  $K$  may describe thermodynamics of the studied system. The other commonly used isotherm is Freundlich isotherm [6]:

$$a = kc^{1/n} \quad (2)$$

where:  $k$  and  $n$  are empirical constants.

For many years parameters of mentioned equations were estimated after linearization. After data were transformed simple linear least squares could have been applied. However, one must note, that such transformation increases error of the estimates and may result in biased parameters [1, 7-9]. Therefore, applying nonlinear regression (NLR) directly to (1) and (2) is welcomed. Typically this procedure requires defining some measure of the distance from the experimental point to a model function [7-9]. In general we can write down that:

$$a_i^{\text{exp}}(c_i) = a_i^{\text{pred}}(\beta, c_i) + \varepsilon_i(c_i, a_i^{\text{exp}}(c_i)) \quad (3)$$

where:  $\beta$  and  $\varepsilon$  stand for the set of the parameters and error function respectively; superscript *exp* means that values were measured experimental, while *pred* means that they are predicted by a model. The optimum estimation of the parameters is achieved when the sum of squares of all error functions is minimized – in other words, the model is closest to experimental points. Figure 1. presents geometrical interpretation of some possible error functions.

Vertical distance is used as an error function the most commonly, mainly due to the fact, that it can be easily computed:

$$a_i^{\text{exp}}(c_i) = a_i^{\text{pred}}(\beta, c_i) + \varepsilon_i^{\text{vert}} \quad (4)$$

However, estimates calculated using vertical distance as an error function are biased towards the steepest region of the estimated function – in case of adsorption isotherm: towards low concentrations [1, 7, 10]. The opposite situation occurs in case of vertical distance – it usually results in

estimates strongly biased towards points located in a high concentration region. Thus, this approach should better predict monolayer capacity.

$$a_i^{\text{exp}}(c_i) = a_i^{\text{pred}}(\beta, c_i - \varepsilon_i^{\text{hor}}) \quad (5)$$

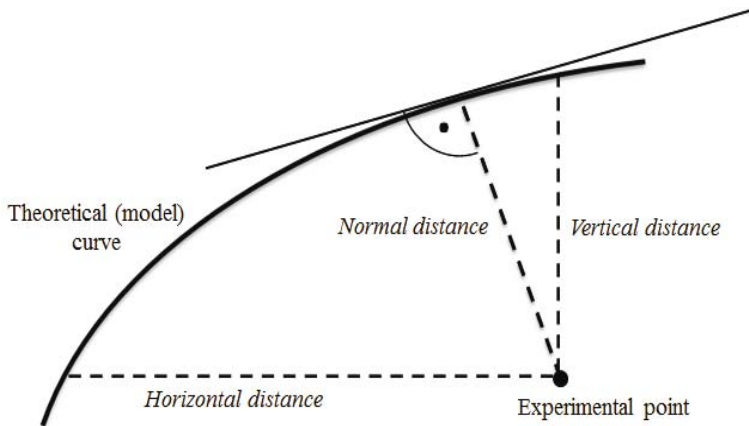


Fig. 1. Geometrical representations of some error functions.

To avoid any bias at all (theoretically) one can use orthogonal distance as an error function according to [1]:

$$\varepsilon_i^{\text{ort}} = \frac{1}{2} \left[ (\varepsilon_i^{\text{ver}})^2 + (\varepsilon_i^{\text{ort}})^2 \right] \quad (6)$$

Some comment is needed at this point. In mathematical formalism equation above does not describe orthogonal distance, but it approximates square of orthogonal distance. To avoid confusion between following paper and [1] it will be still called orthogonal. The true orthogonal distance (distance from the experimental points to a closest point of the model isotherm) and its' square are called normal and squared normal, respectively. Normal error is given by:

$$\varepsilon_i^{\text{norm}} = \min \left\{ d \left( (a_i^{\text{exp}}, c_i), (x, y) \in \text{isotherm} \right) \right\} \quad (7)$$

The goal of this work is examine which of the proposed measures of an error is the most efficient for fitting data to Langmuir and Freundlich model. One must have in mind that nonlinear regression is most credible when following assumptions are justified:

- expected value of errors is zero (verified via t-Student test) [11];
- errors are homoscedastic, which means that they have constant variance (verified via error vs. score plot);
- errors are normally distributed (verified via Shapiro-Wilk test) [11] and uncorrelated.

Violation of these assumptions may potentially lead to misleading results.

## 2. EXPERIMENTAL

Data sets were experimental adsorption isotherms of L-phenylalanine (>99.9%, SigmaAldrich) on graphite (SigmaAldrich). Each isotherm consists of at least 20 experimental points (each obtained from 3 to 6 replicates). Concentration of all solutions (before and after adsorption) were measured with Carry 100 UV-Vis spectrometer by Varian at wavelength 206 nm.

Single replicate was done according to a following procedure. 10mL of a solution of L-phenylalanine in a borate buffer was added to 0.20g of graphite in an Erlenmeyer flask. The suspension was shaken (120 osc./min) for 30 minutes to equilibrate and after that the solid was filtrated on a cellulose filter. Postadsorption concentration was measured via UV-Vis spectroscopy. A pH was equal to 6.1, 8.1 and 10.0; in all cases concentration of the buffer was constant and equal to 0.075 mol/dm<sup>3</sup>. The ionic strength was also kept constant and was equal to 0.1 mol/dm<sup>3</sup> in all experiments.

Optimization procedure was performed with Newton-Raphson algorithm with multistart (1000 different initial points in a range  $\pm 50\%$  of optimal parameters). We did not weight experimental points with their uncertainties despite the fact that they have been precisely calculated.

Due to the experimental method adsorption and concentration errors are not independent. However, most of the adsorption experiments are performed in a similar way, therefore, we believe that our results might be helpful for some researchers.

## 3. RESULTS AND DISCUSSION

In Table 1. we have presented best estimates of the parameters of equations (1) and (2) depending on the type of error function. First thing to notice is a fact, that in case of Langmuir isotherm vertical error

function always gives the smallest monolayer capacity  $a_m$ . At the same time the biggest values of this parameter are obtained when error function is defined as horizontal distance from point to isotherm. A relative standard deviation (RSD) was calculated for each parameter to evaluate its' sensitivity to type of error function. In all 3 Langmuir isotherms higher variability was observed for  $K$  than  $a_m$ , therefore we postulate, that thermodynamic constant is a parameter more sensitive to the choice of error function. In case of Freundlich equation there is almost no sensitivity of  $k$  on the type of error function applied in optimization. It is interesting to notice, that orthogonal and squared normal error function leads to almost exactly the same results in both Langmuir and Freundlich equation.

Table 1. Best estimates of the parameters of the isotherm.

	vertical	horizontal	orthogonal	normal	squared normal	RSD
Langmuir, pH = 6.1						
$a_m$	9.612	10.22	9.691	10.13	10.22	0.032
$K$	2.477	2.106	2.504	2.136	2.105	0.091
Langmuir, pH = 8.1						
$a_m$	9.989	11.14	10.06	11.05	11.13	0.056
$K$	2.268	1.735	2.299	1.809	1.725	0.148
Langmuir, pH = 10.0						
$a_m$	5.143	5.643	5.396	5.470	5.581	0.036
$K$	2.626	2.232	2.497	2.232	2.235	0.079
Freundlich, pH = 6.1						
$k$	6.810	6.858	6.903	6.829	6.858	0.005
$n$	2.045	2.211	2.060	2.197	2.203	0.039
Freundlich, pH = 8.1						
$k$	6.846	6.883	6.853	6.973	6.884	0.007
$n$	1.982	2.143	1.985	2.062	2.148	0.039

cont. Table 1.

Freundlich, pH = 10.0						
$k$	3.799	3.865	3.898	3.839	3.861	0.009
$n$	1.951	2.000	1.937	2.000	1.989	0.015

Despite the fact, that some parameters may differ by as much as 12 % depending on the error function, plots of model isotherms are very similar to each other (see Figure 2 and Figure 3).

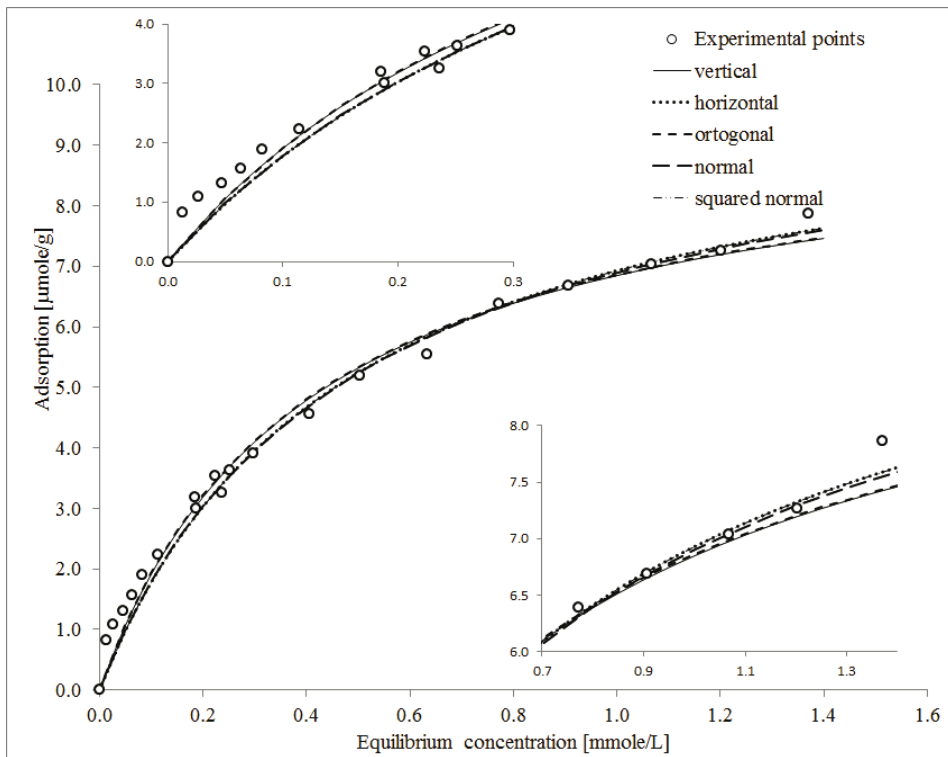


Fig. 2. Plots of optimized Langmuir isotherms for different error functions (pH = 6.1).

In all cases t-Student test confirmed that mean value of the error is equal to zero (at 95 % confidence interval). The homoscedasticity of the residuals is discussed on the basis of plots similar to Figure 4. and Figure 5. The errors are homoscedastic when there are neither patterns on the plot (residuals are not grouped) neither outliers. In case of Langmuir model in the pH = 6.1, see Figure 4., one can see a possible outlier (observation number 17) on all plots and a possible pattern (observations

1-8 have same sign), which makes a homoscedastic assumption speculative. For Freundlich isotherm in  $\text{pH} = 6.1$  we did not observe such obvious outliers and the pattern is less significant, especially when we apply orthogonal error function. This suggested that in this case we were dealing with a homoscedastic error.

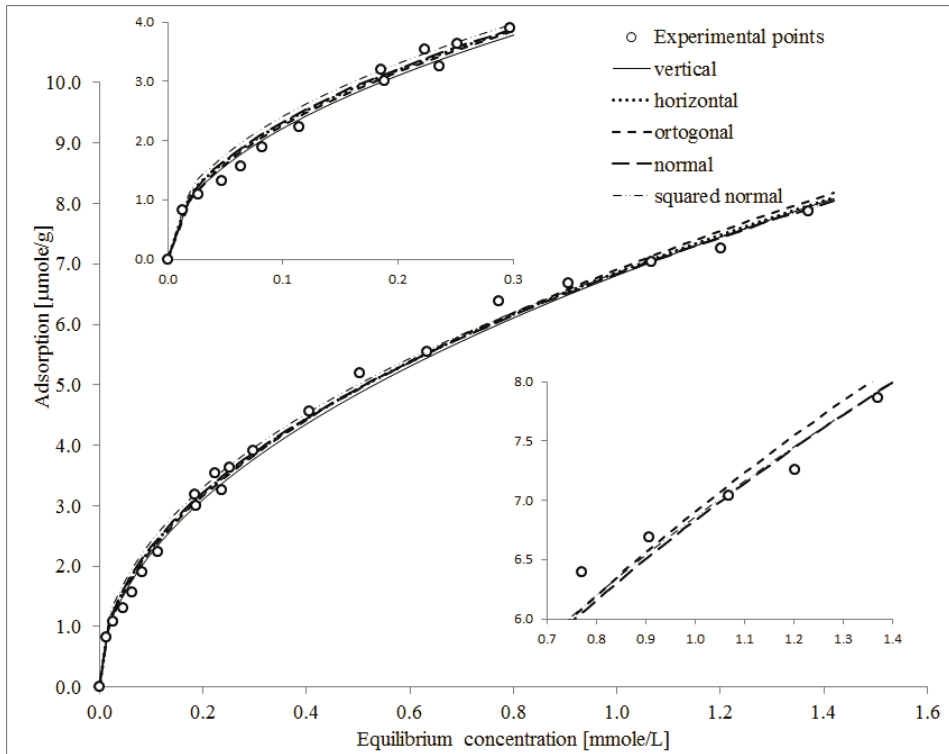


Fig. 3. Plots of optimized Freundlich isotherms for different error functions ( $\text{pH} = 6.1$ ).

A Figure 6. presents a bar plot of p-values of Shapiro-Wilk test for normality of the distribution of an error. In general we can say, that the lower the p-value the less Gaussian is the distribution. It is clear that in this example change of the error function from vertical to orthogonal ‘improved normality’ in case of Freundlich isotherm but totally ‘destroyed’ it in case of Langmuir model.

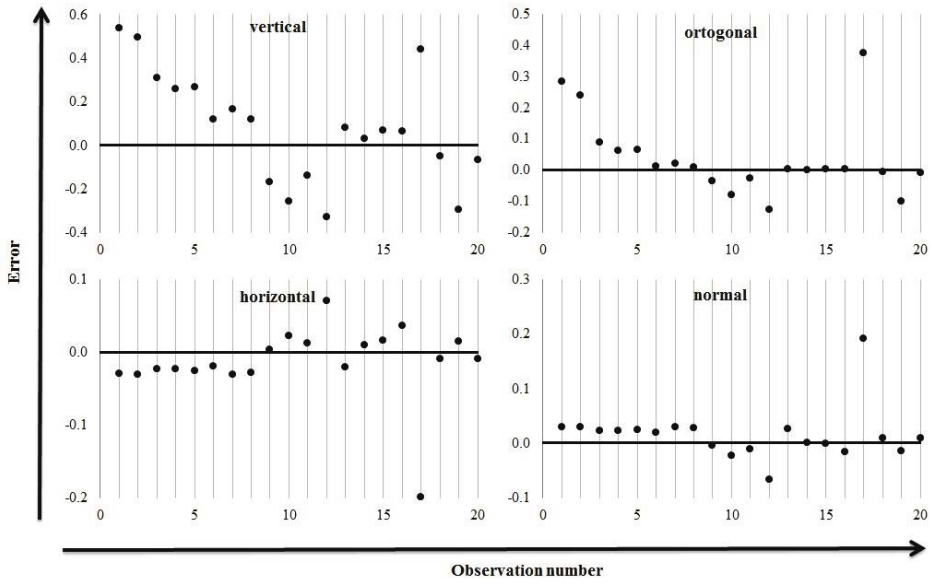


Fig.4. Residuals (errors) of the best estimate Langmuir model (pH = 6.1).

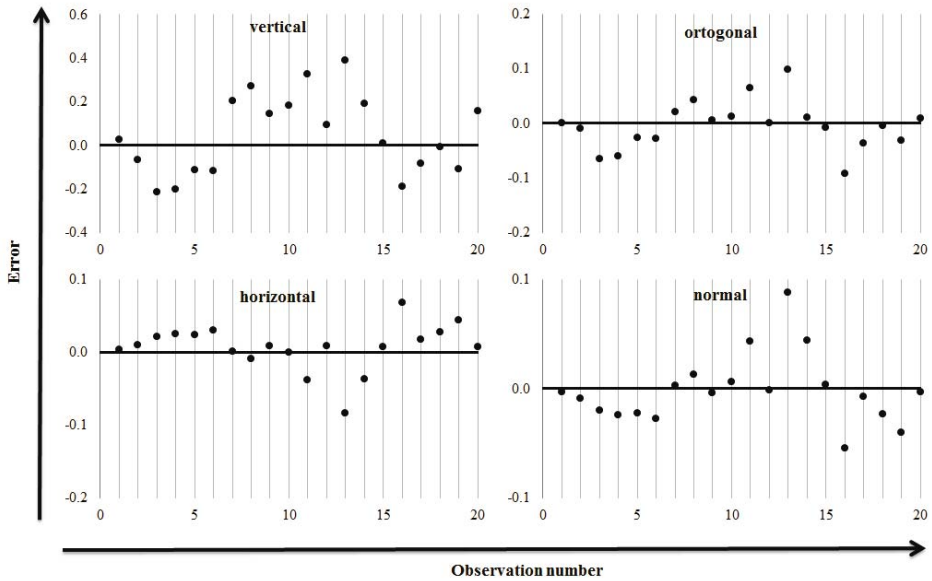


Fig. 5. Residuals (errors) of the best estimate Freundlich isotherm (pH = 6.1).



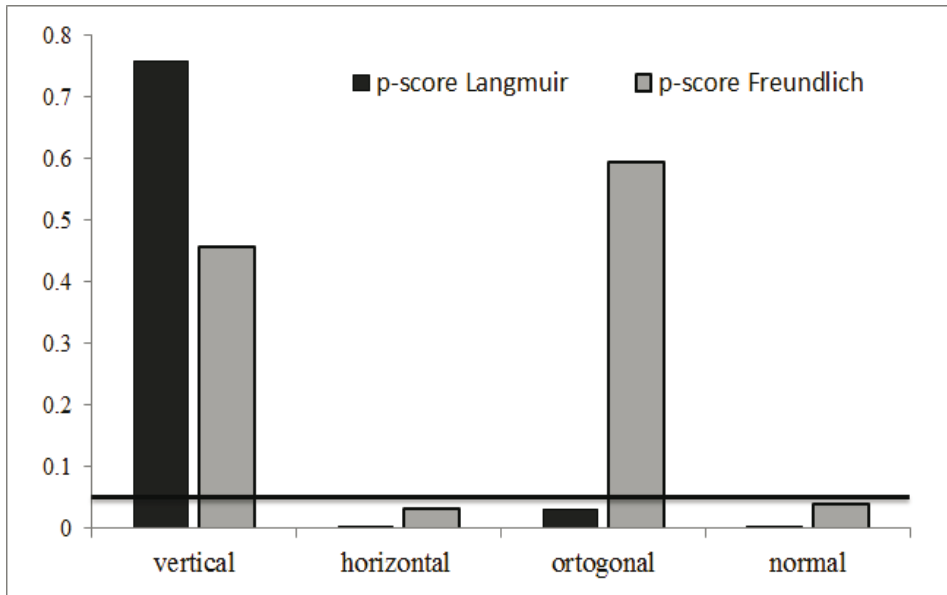


Fig. 6. p-scores of Shapiro-Wilk test for normality of the residuals (errors); (pH = 6.1).

Summing up the all results mentioned, the most reliable isotherm to describe experimental data of adsorption of L-phenylalanine on graphite in pH=6.1 seems to be Freundlich isotherm with the ortogonal error function. It is so because for this choice errors are normally distributed, homoscedastic and their expected value is equal to 0 at 95% confidence interval.

It has to be said, that this choice is not universal not only for studied system but even for different model applied to the same experimental data. However, we have showed that changing the error function might be a very useful tool in analysis of experimental data. It allows to change properties of the regression analysis without changing the studied model, and therefore increase data reliability.

In case of 'permanent' heteroscedasticity of the residuals very efficient is so-called 'robust regression' [7-8]. It can be easily implemented to an algorithm and its' application will be discussed in our future papers.

Presented approach is only a small piece of a complex data analysis proecdure. The following steps should include confidence interval parameters estimation for fitted parameters and calculating goodness of fit coefficients [9, 12-15]. Moreover, various procedures of optimization

may be examined, bias should be discussed as well as robustness should be introduced. This topics will be discussed in subsequent articles.

#### 4. CONCLUSIONS

We have studied the effect of the form of error functions on the properties of the regression analysis of a set of experimental data. The conclusions are following:

1. Results confirm that vertical error function is biased towards region of low equilibrium concentrations, opposite to horizontal error function;
2. Langmuir isotherm seems to be more sensitive to the error function type;
3. There are no universal correlations between form of error function and general properties of regression – optimization is a necessity for every data set;
4. Changing an error function may be a very useful tool allowing one to increase data analysis reliability.

#### REFERENCES

- [1] M. I. El-Khaiary, *Journal of Hazardous Materials*, **158**, 73, (2008).
- [2] T. Robinson et al., *Bioresource Technology*, **77**, 247, (2001).
- [3] Y. S. Ho et al., *Process Biochemistry*, **40**, 119, (2005).
- [4] G. McKay et al., *Water Air Soil Pollution*, **114**, 423, (1999).
- [5] I. Langmuir, *Journal of the American Chemical Society*, **38**, 2221, (1916).
- [6] H. M. F. Freundlich, *Zeitschrift für Physikalische Chemie*, **57**, 385, (1906).
- [7] S. Chatterjee and J. S. Simonoff, “*Handbook of Regression Analysis*”, John Wiley and Sons, New Jersey, 2013.
- [8] N. R. Draper and H. Smith, “*Applied Regression Analysis*”, John Wiley and Sons, New York, 1998.
- [9] “*Measurement Error in Nonlinear Models. A Modern Perspective*”, Monographs on Statistics and Applied Probability, **105**, Taylor and Francis Group, Boca Raton, 2006.
- [10] M. Hadi et al., *Chemical Engineering Journal*, **160**, 408, (2010).

- [11] M. Walesiuk and E. Gantar, “*Statystyczna analiza danych z wykorzystaniem programu R*”, Wydawnictwo Naukowe PWN, Warszawa, 2012.
- [12] H.-T. Thai et al., *Journal of Pharmacokinetics and Pharmacodynamics*, **41**, 15, (2014).
- [13] A. Spiess and N. Neumayer, *BioMed Central Pharmacology*, **10**, 6, (2010)
- [14] W. C. Rooney and L. T. Biegler, *Process Systems Engineering*, **47**, 1794, (2001).

### CURRICULA VITAE

**Dawid Myśliwiec** was born in Lublin in 1988. He studied Basic and Applied Chemistry at Maria Curie-Skłodowska University in Lublin. In 2012 he obtained M.Sc. degree based on master thesis entitled: “A research on the influence of magnetic field on adsorptive properties of the system: hematite – aqueous solution of polyethyleneimine”, supervised by prof. Stanisław Chibowski. Since 2012 he is a Ph.D. Chemistry student at Maria Curie-Skłodowska University in Lublin.



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