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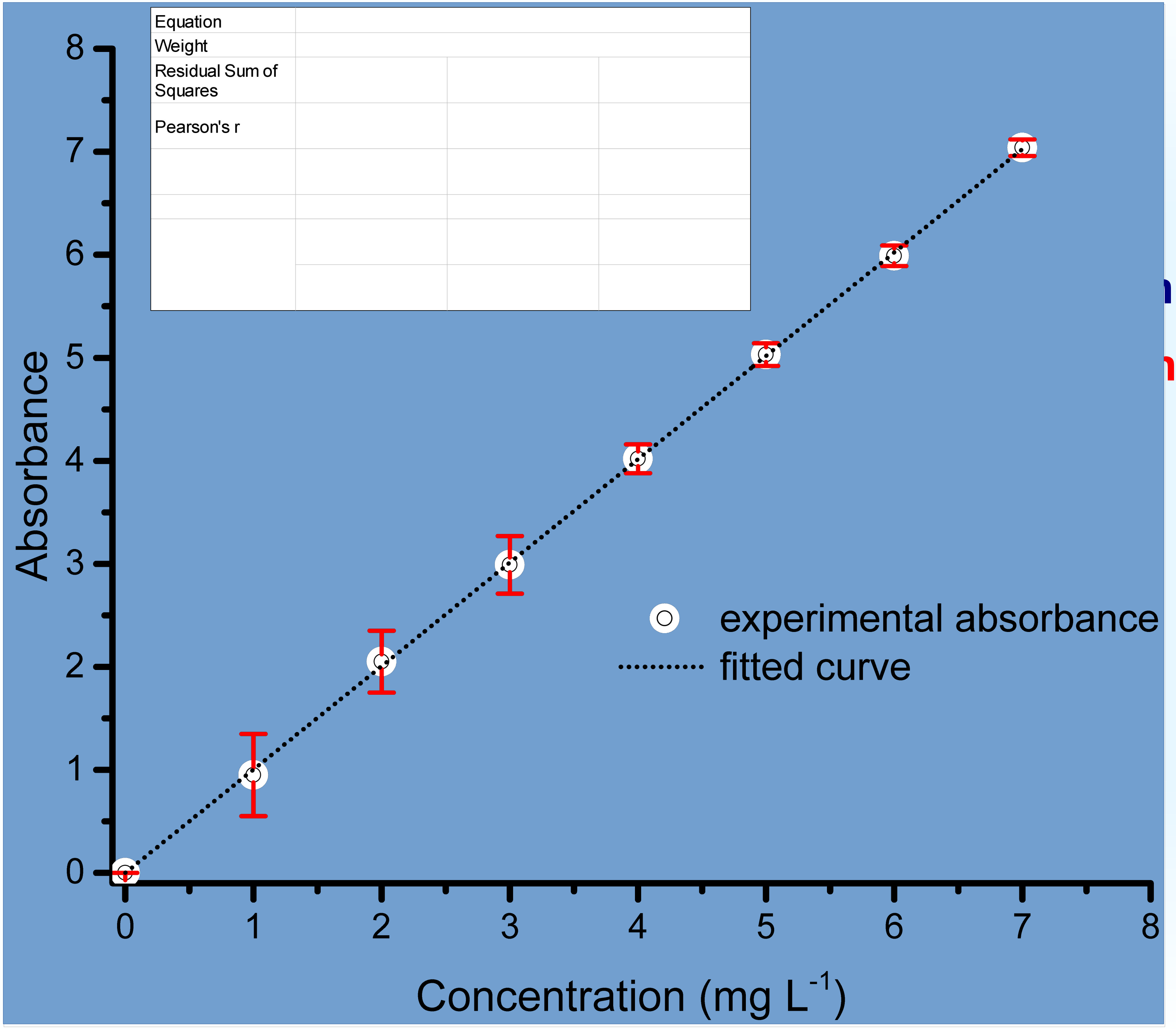
Linear and nonlinear fitting of isotherms and kinetics of adsorption

The misuse of linearization is probably the most common error in data analysis of adsorption studies. It was largely used some decades ago when computers and statistical software were not available. Presently, linearization in data analysis is on the increase because the authors usually employ the simplest tool to analyze their experimental data. One of the reasons for using linear equations is the possibility of performing less experimental points to define a line (that is the major problem of using nonlinear equations, which require more experimental points to define a curve) or alternatively, discard some points to increase the R^2 values. The main problem is that some points are discarded to increase the R^2 values, and the authors are not concerned about the values of the parameters of the equilibrium and kinetic of adsorption models.

Linear and nonlinear fitting of isotherms and kinetics of adsorption

There are problems associated with linearizing an inherently nonlinear equation using various transformations. The main concern when transforming data to obtain a linearized equation is the knowledge of the error-structure of the data and how this structure is affected by the mathematical manipulation of the data. The linearization is based on the fact that the variance of all *q* values (Y variable of the graph; dependent variable; amount of adsorbate adsorbed by the adsorbent) is equal for all range of the data. By assuming homoscedasticity of the data (assuming equal variance for all q values throughout the range of the data) when it is actually heteroscedastic (the variance of all q values are not equal in the full range of the data), may result in overestimating the goodness of fit as measured by the correlation coefficient (*R*), which translates into error in the coefficient of determination and also in the adjusted coefficient of determination. Therefore, higher R^2 values do not necessarily means better fit of the experimental data.



ncentration

ndard error

Therefore for low concentrations of the adsorbate, the variance of sorption capacity (q, Y axis) is not uniform for all values of q measured during the experiments of na equilibrium isotherm as well as an kinetic of adsorption.

$$q = \frac{(C_o - C_f).V}{m}$$

Low concentration

High uncertainty

Linear and nonlinear fitting of isotherms and kinetics of adsorption

In practice, authors have to delete some points from their curves to justify the linearization procedure. This adjustment decreases the degree of freedom (DOF) of the fitting model, which consequently decreases the number of independent ways by which a dynamic system can move without violating any constraint imposed on it. The degree of freedom can be defined as the minimum number of independent coordinates that can specify the position of a system completely. In order to make it clear to the readers, some case studies will be discussed below.

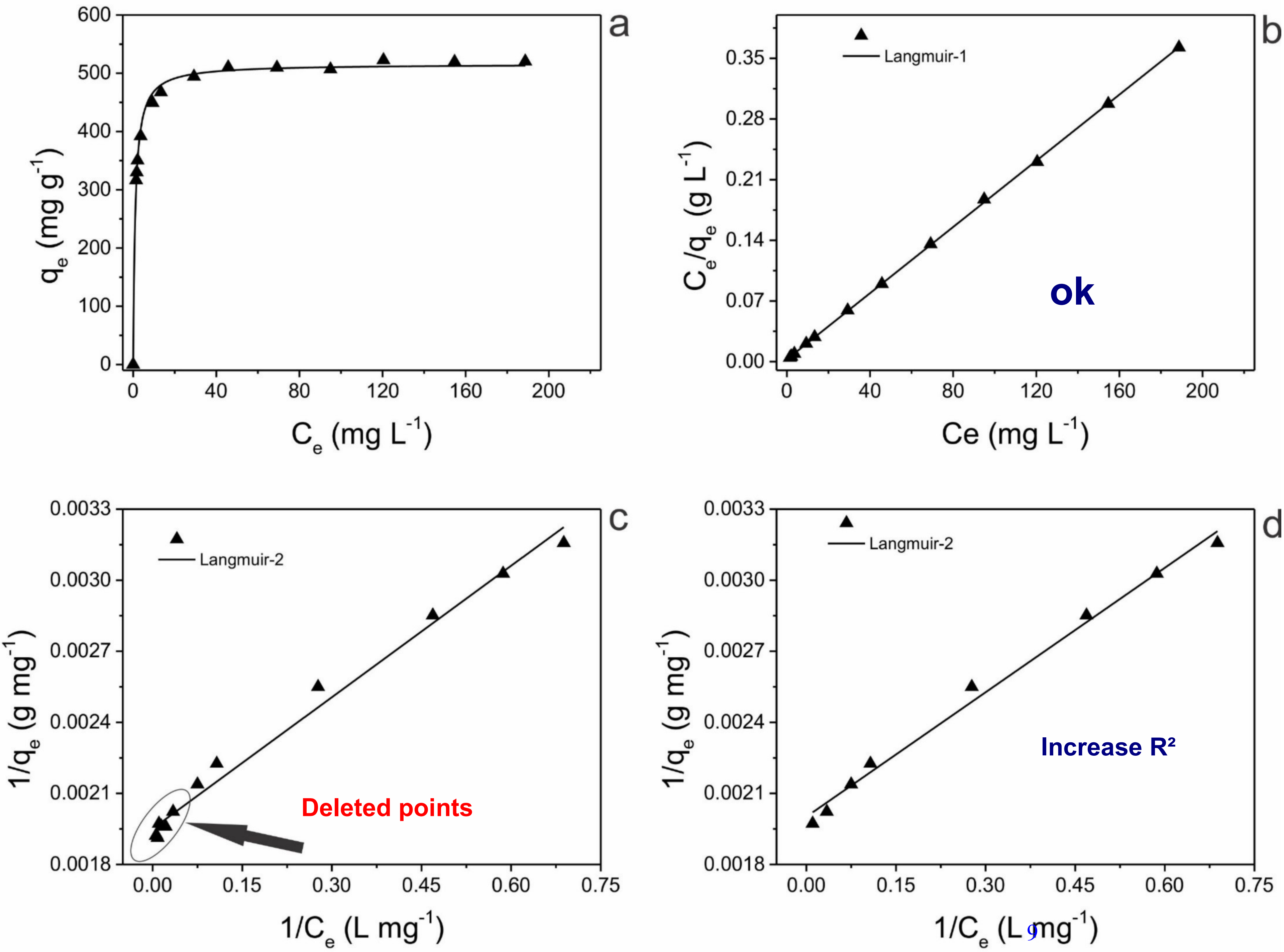
Linear forms of Langmuir isotherm

Isotherm Moc		
$q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_{\max}} + \frac{1}{Q_{\max}} C_e$	$\frac{C_e}{q_e}$ vs C_e
	$\frac{1}{q_e} = \frac{1}{Q_{\max}} + \left(\frac{1}{K_L \cdot Q_{\max}} \right) \frac{1}{C_e}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
	$q_e = Q_{\max} - \left(\frac{1}{K_L} \right) \frac{q_e}{C_e}$	q_e vs $\frac{q_e}{C_e}$
	$\frac{q_e}{C_e} = K_L \cdot Q_{\max} - K_L \cdot q_e$	$\frac{q_e}{C_e}$ vs q_e

Experimental V

C_e (mg L^{-1})	q_e
0.0000	0.

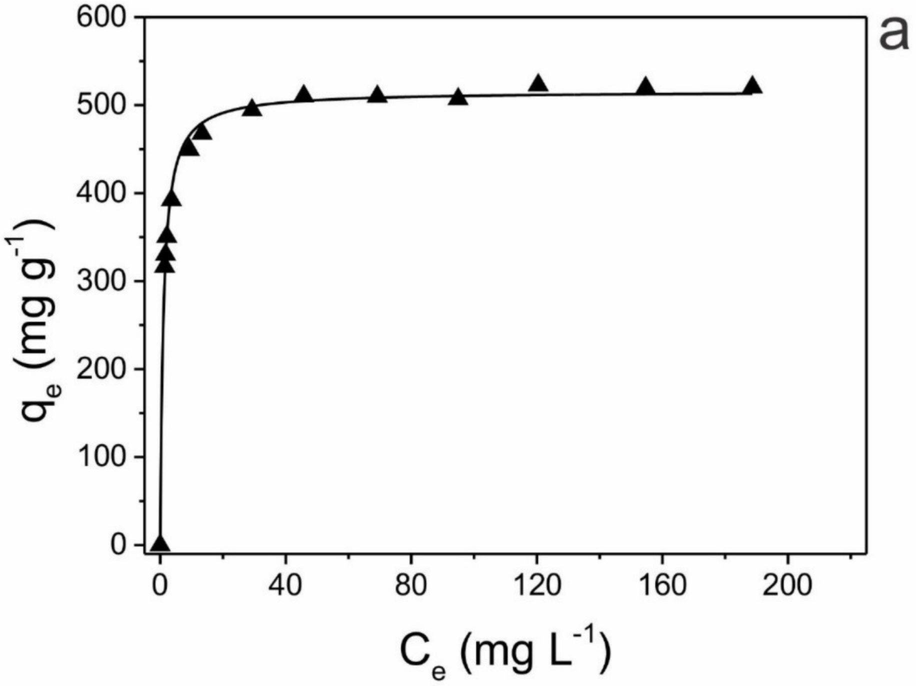
The point $q_{e=0}$ for Ce = 0 is disregarded in the linearized methods



ok

Deleted points

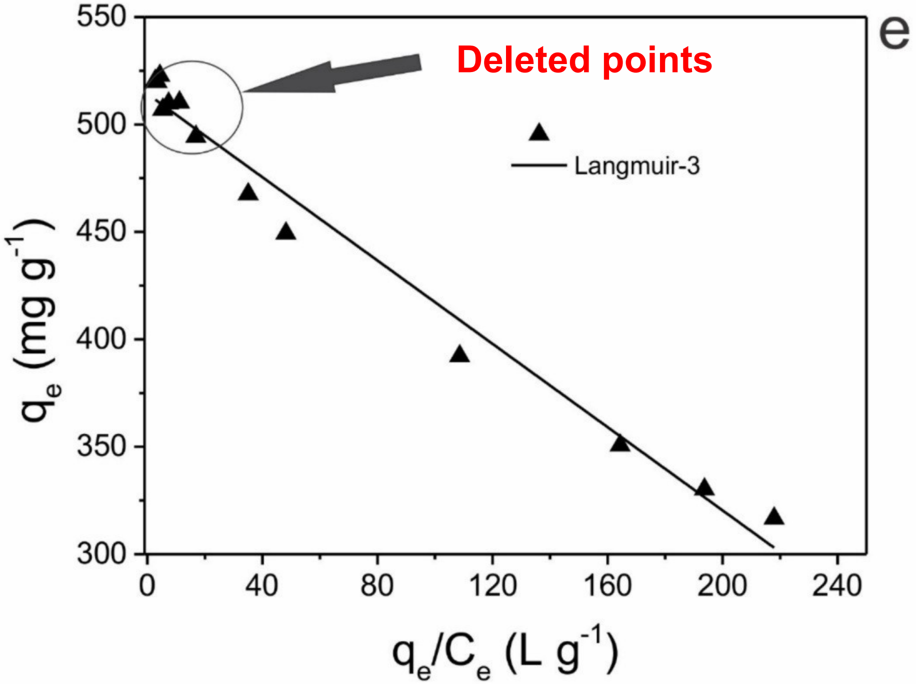
Increase R²

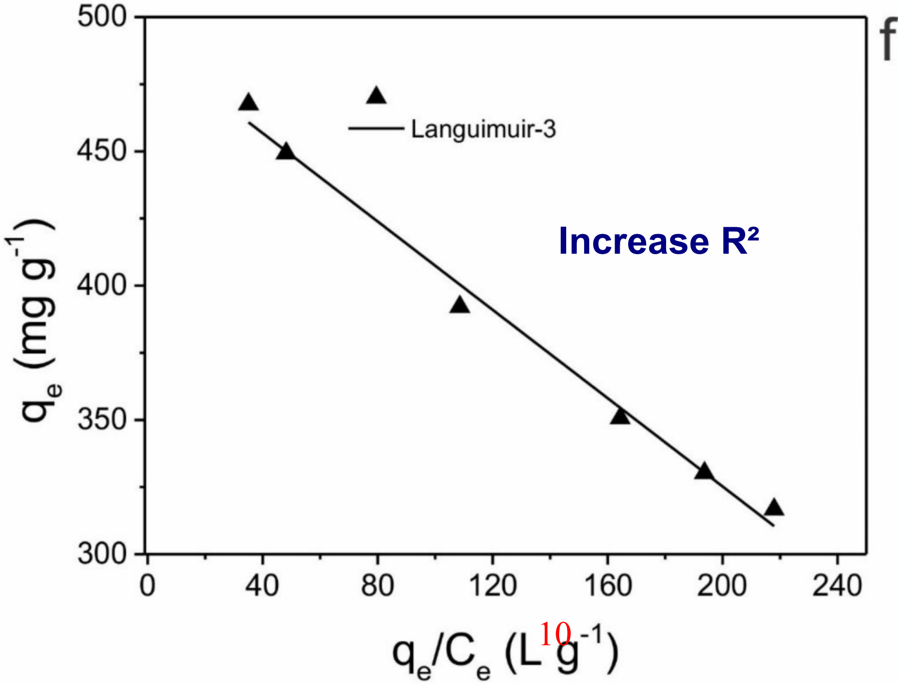


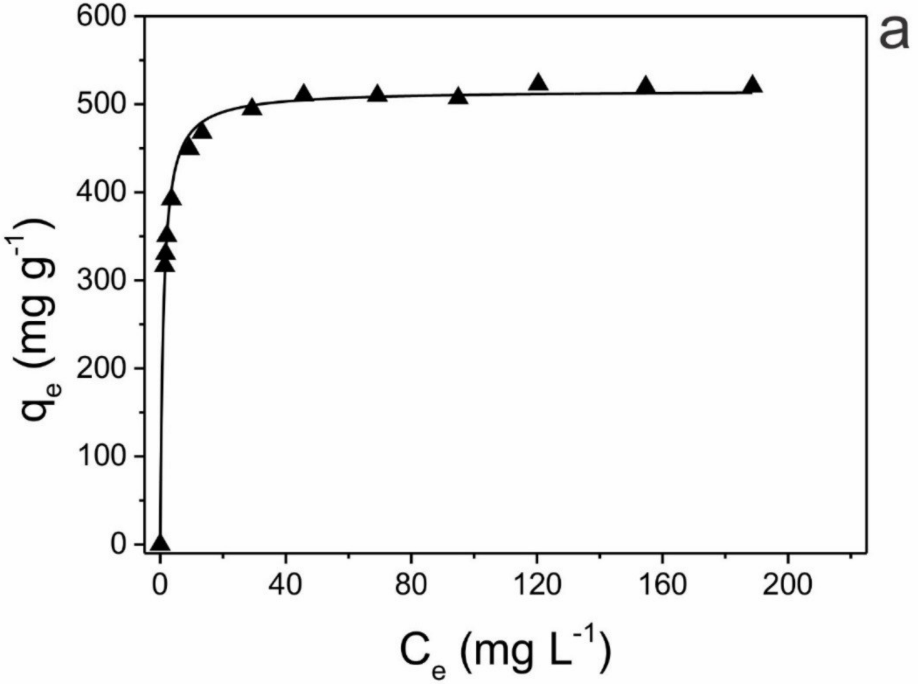
$$R^2 = \left(\frac{\sum_i^n \left(q_{i,exp} - \bar{q}_{exp}\right)^2 - \sum_i^n \left(q_{i,exp} - q_{i,model}\right)^2}{\sum_i^n \left(q_{i,exp} - \bar{q}_{exp}\right)^2} \right)$$

$$R^2_{adj} = 1 - \left(1 - R^2\right) \cdot \left(\frac{n-1}{n-p-1} \right)$$

$$SD = \sqrt{\left(\frac{1}{n-p} \right) \cdot \sum_i^n \left(q_{i,exp} - q_{i,model}\right)^2}$$



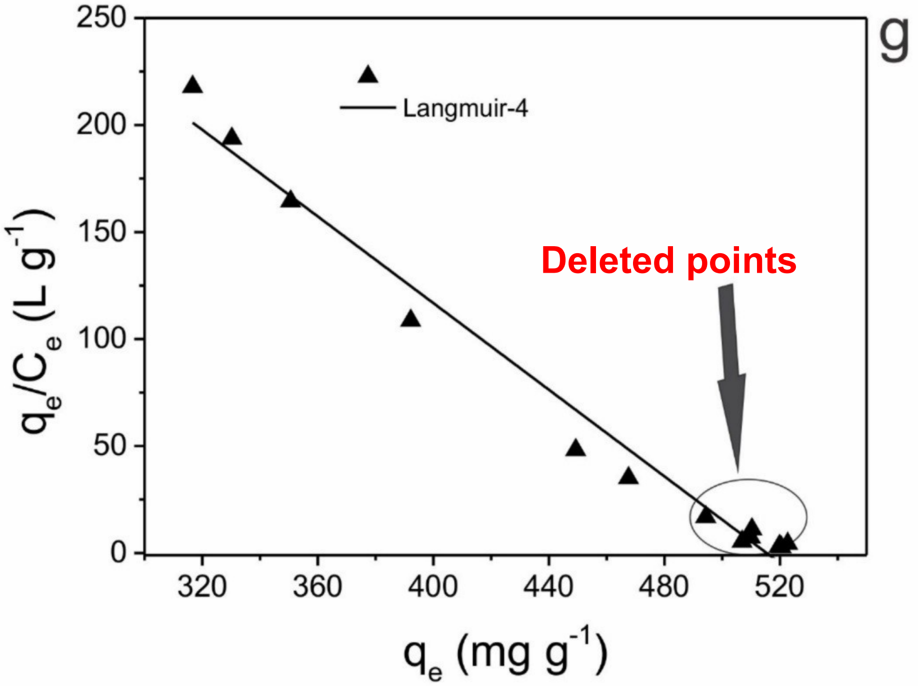




$$R^2=\left(\frac{\sum_i^n\left(q_{i,exp}-\overline{q}_{exp}\right)^2-\sum_i^n\left(q_{i,exp}-q_{i,model}\right)^2}{\sum_i^n\left(q_{i,exp}-\overline{q}_{exp}\right)^2}\right)$$

$$R^2_{adj}=1-\left(1-R^2\right)\cdot\left(\frac{n-1}{n-p-1}\right)$$

$$SD=\sqrt{\left(\frac{1}{n-p}\right)\cdot\sum_i^n\left(q_{i,exp}-q_{i,model}\right)^2}$$



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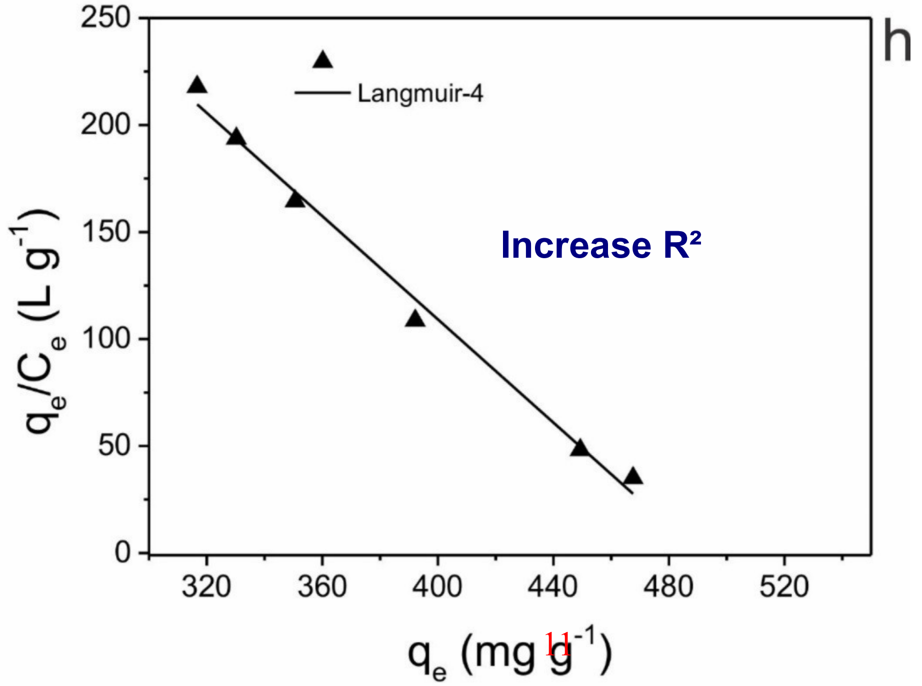


Increase R²

Parameter	**value**	**Parameter**	**value**
Nonlinear	Fig. 4.16 (a)	Langmuir-1	Fig. 4.16 (b)
Q_{max} (mg g^{-1})	515.8	Q_{max} (mg g^{-1})	523.7
K_L (L mg^{-1})	0.9966	K_L (L mg^{-1})	0.7252
Number of Points	14	Number of Points	13
Degrees of Freedom	12	Degrees of Freedom	11
Reduced Chi-Sqr (mg g^{-1})	84.13	Reduced Chi-Sqr (g L^{-1})	$1.818.10^{-6}$
Res. Sum of Squ. (mg g^{-1})^2	1009	Res. Sum of Squ. (g L^{-1})^2	$1.999.10^{-5}$
R (COC)	0.9981	R (COC)	0.9999
R^2 (COD)	0.9962	R^2 (COD)	0.9999
R^2_{Adj}	0.9959	R^2_{Adj}	0.9999
SD (mg g^{-1})	9.172	SD (g L^{-1})	$1.348.10^{-3}$

Langmuir-2

Q_{max} (mg g^{-1})
K_L (L mg^{-1})

Langmuir-3
Q_{max} (mg g^{-1})

$$R^2=\left(\frac{\sum_i^n\left(q_{i,exp}-\bar{q}_{exp}\right)^2-\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2}{\sum_i^n\left(q_{i,exp}-\bar{q}_{exp}\right)^2}\right)$$

$$RSS=\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2$$

$$R^2_{adj}=1-\left(1-R^2\right).\left(\frac{n-1}{n-p-1}\right)$$

$$SD=\sqrt{\left(\frac{1}{n-p}\right).\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2}$$

Langmuir-4	Fig. 4.16 (g)	Langmuir-4	Fig. 4.16 (h)
Q_{max} (mg g^{-1})	515.4	Q_{max} (mg g^{-1})	490.6
K_L (L mg^{-1})	1.012	K_L (L mg^{-1})	1.206
Number of Points	13	Number of Points	6
Degrees of Freedom	11	Degrees of Freedom	4
Reduced Chi-Sqr (L g^{-1})	131.5	Reduced Chi-Sqr (L g^{-1})	61.17
Residual Sum of Squ. (L g^{-1})^2	1446	Residual Sum of Squ. (L g^{-1})^2	244.7
R (COC)	0.9905	R (COC)	0.9958
R^2 (COD)	0.9810	R^2 (COD)	0.9916
R^2_{Adj}	0.9793	R^2_{Adj}	0.9895
SD (L g^{-1})	11.47	SD (L g^{-1})	7.821

$$R^2=\left(\frac{\sum_i^n\left(q_{i,exp}-\bar{q}_{exp}\right)^2-\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2}{\sum_i^n\left(q_{i,exp}-\bar{q}_{exp}\right)^2}\right)$$

$$RSS=\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2$$

$$R^2_{adj}=1-\left(1-R^2\right).\left(\frac{n-1}{n-p-1}\right)$$

$$SD=\sqrt{\left(\frac{1}{n-p}\right).\sum_i^n\left(q_{i,\,exp}-q_{i,\,model}\right)^2}$$

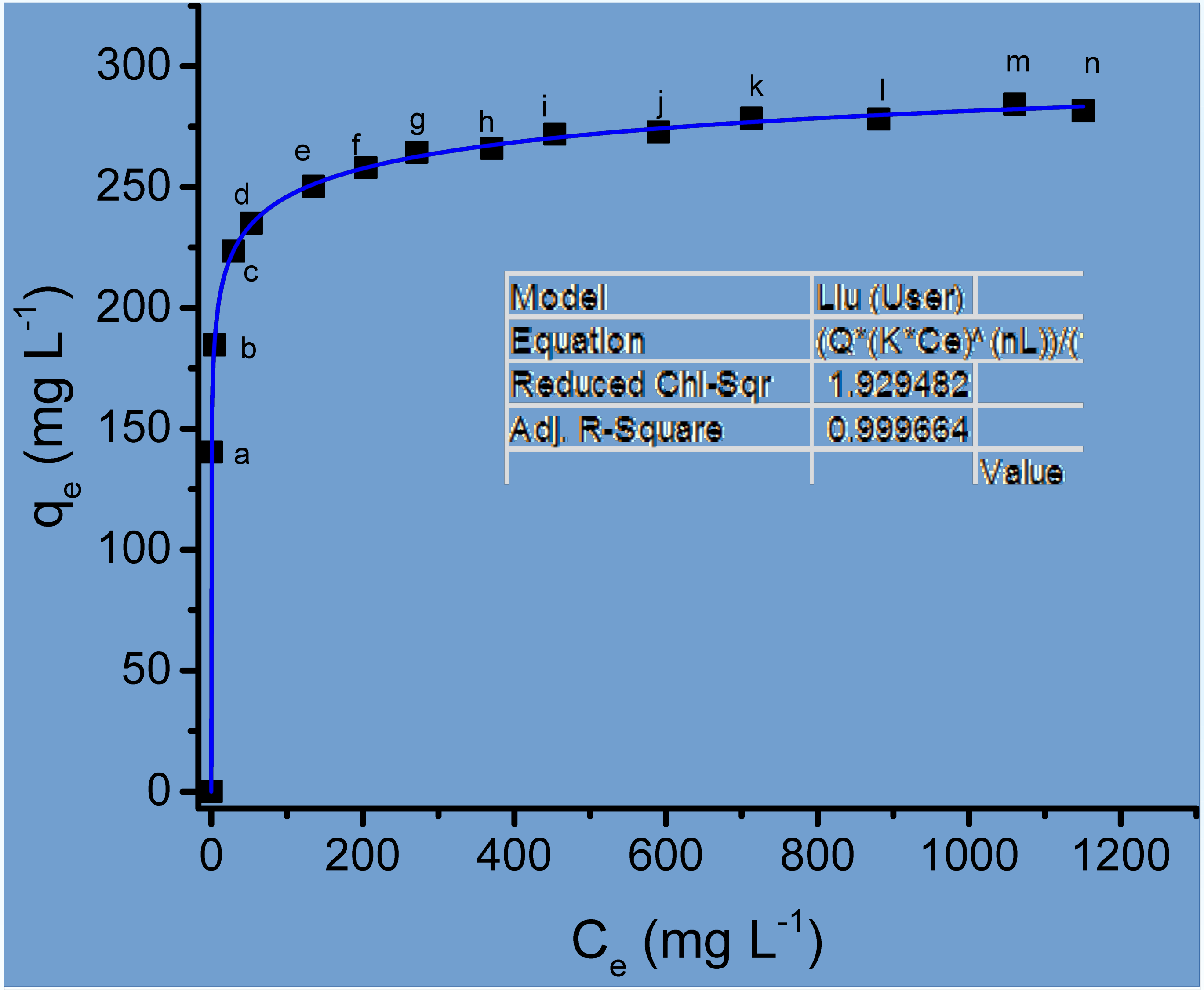
Table 4.5. Relative differences of Q_{max} and K_L isotherm parameters of linearized Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4 in relation to nonlinear Langmuir equation. The values are expressed as percentage

After deleting some points to increase

The values of R²

Considering that K_L values are very important equilibrium parameter for estimating equilibrium constants (determination of thermodynamic parameters) the use of Langmuir-1 linearized isotherms could lead to erroneous estimation of Gibb's free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of adsorption.

Thermodynamics of Adsorption



Model	Liu (User)	
Equation	((Q*(K*Ce)^(nL))/(	
Reduced Chi-Sqr	1.929482	
Adj. R-Square	0.999664	
		Value

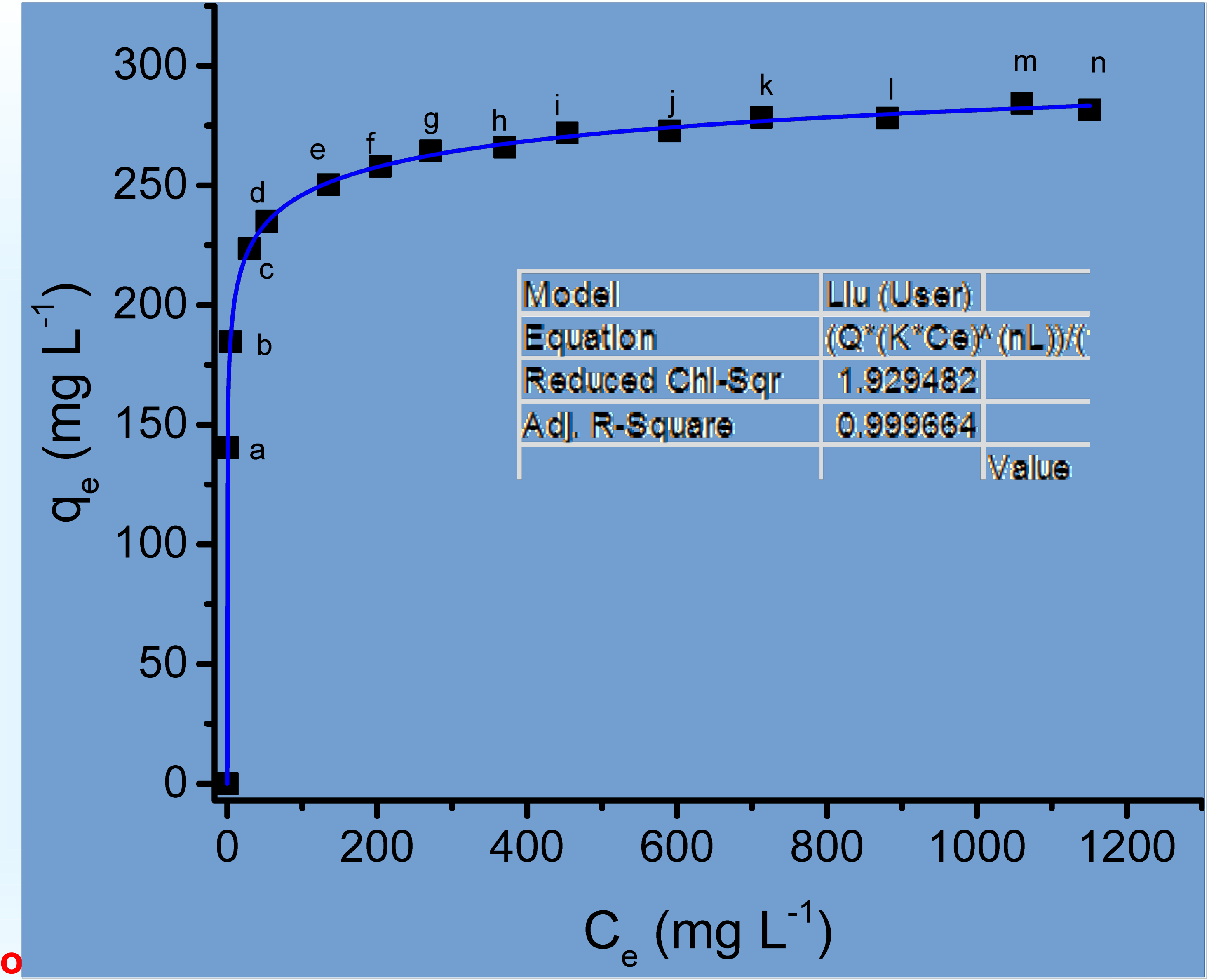
Point	Co (mg/				
	0				

T 25°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}



Model	Liu (User)	
Equation	((Q*(K*Ce)^(nL))/(	
Reduced Chi-Sqr	1.929482	
Adj. R-Square	0.999664	
		Value

T 25°C,

adsorbent: Avo

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}

Point	Co (mg/L				
	0				

T 30°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}

Point	Co (mg/				
	0				

T 35°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}

Point	Co (mg/				
	0				

T 40°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}

Point	Co				
	0				

T 45°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

Adsorbent dosage: 1.5 g L^{-1}

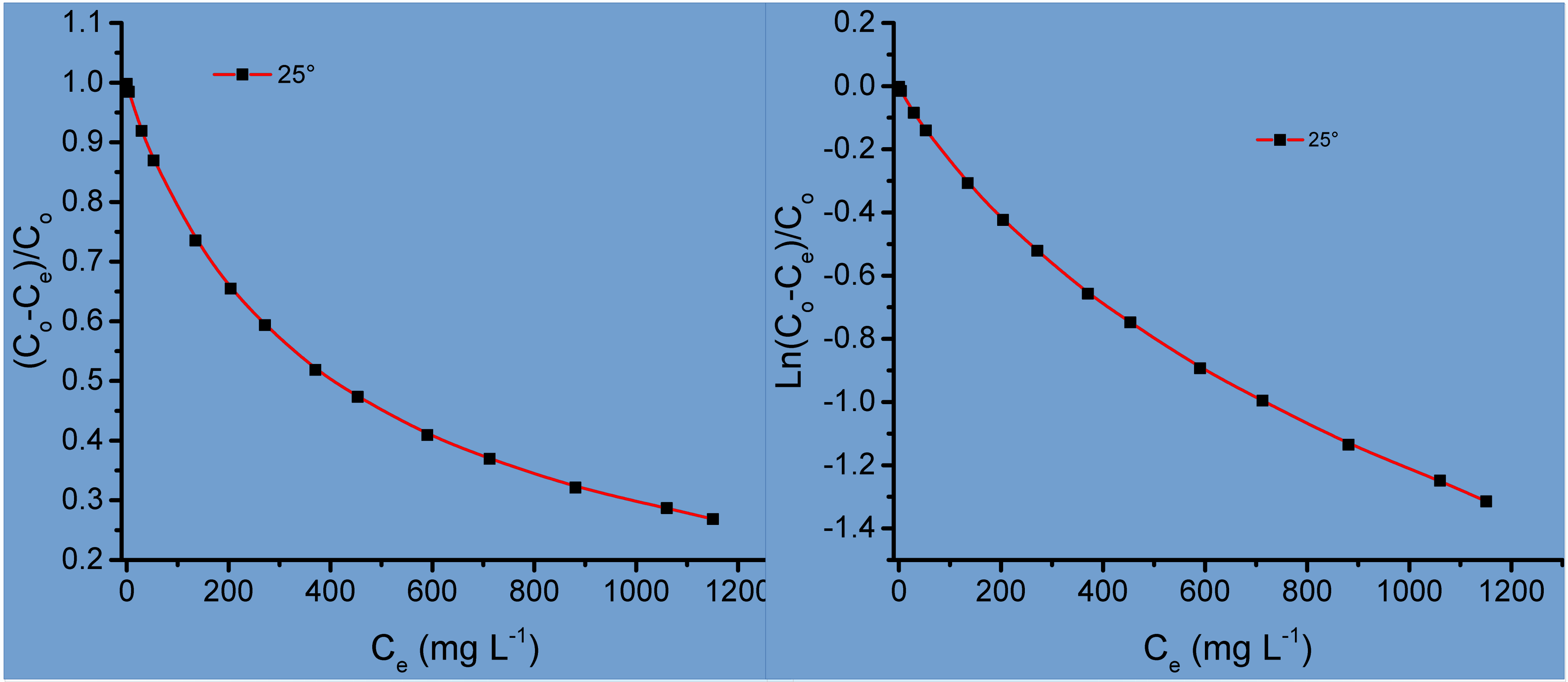
Point	Co				
	0				

T 50°C,

adsorbent: Avocado seed activated carbon

Adsorbate: 3 aminophenol;

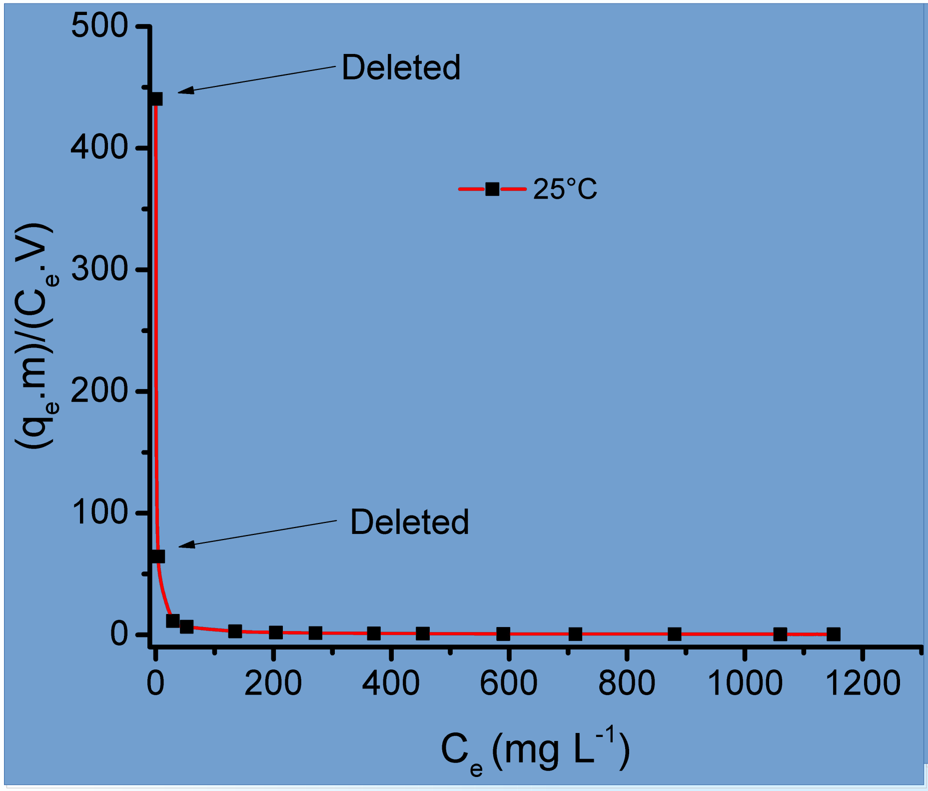
Adsorbent dosage: 1.5 g L^{-1}

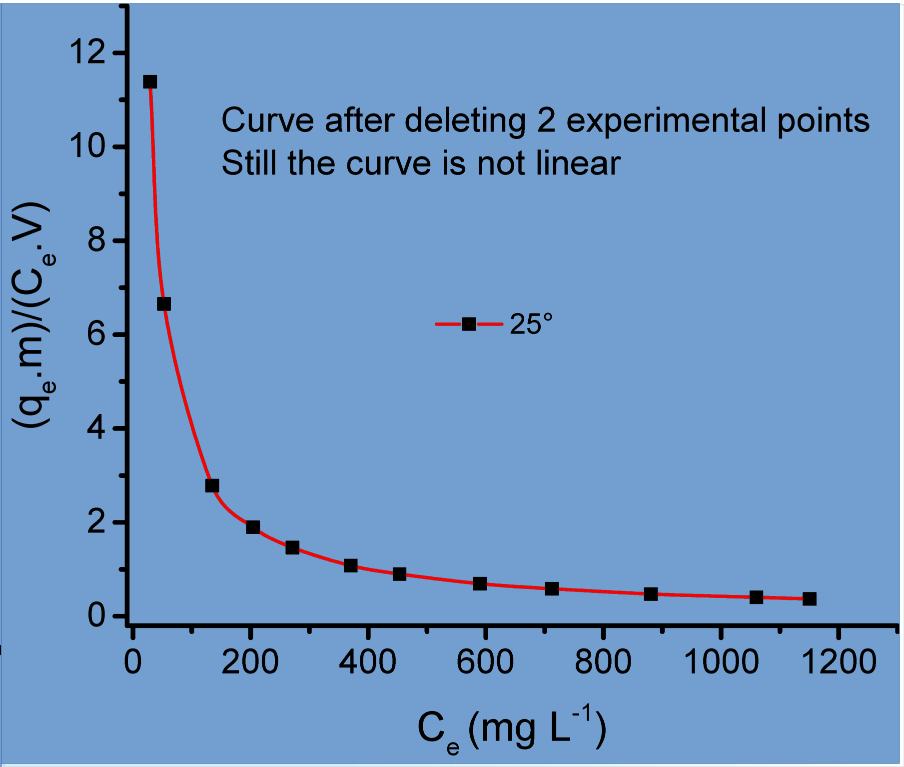


Even applying Ln to the ratio $(C_{o-Ce})/Co$ this is not linearized

Therefore at low Ce concentrations, it is possible to obtain a

“*Supposed*” value of Kequilibrium

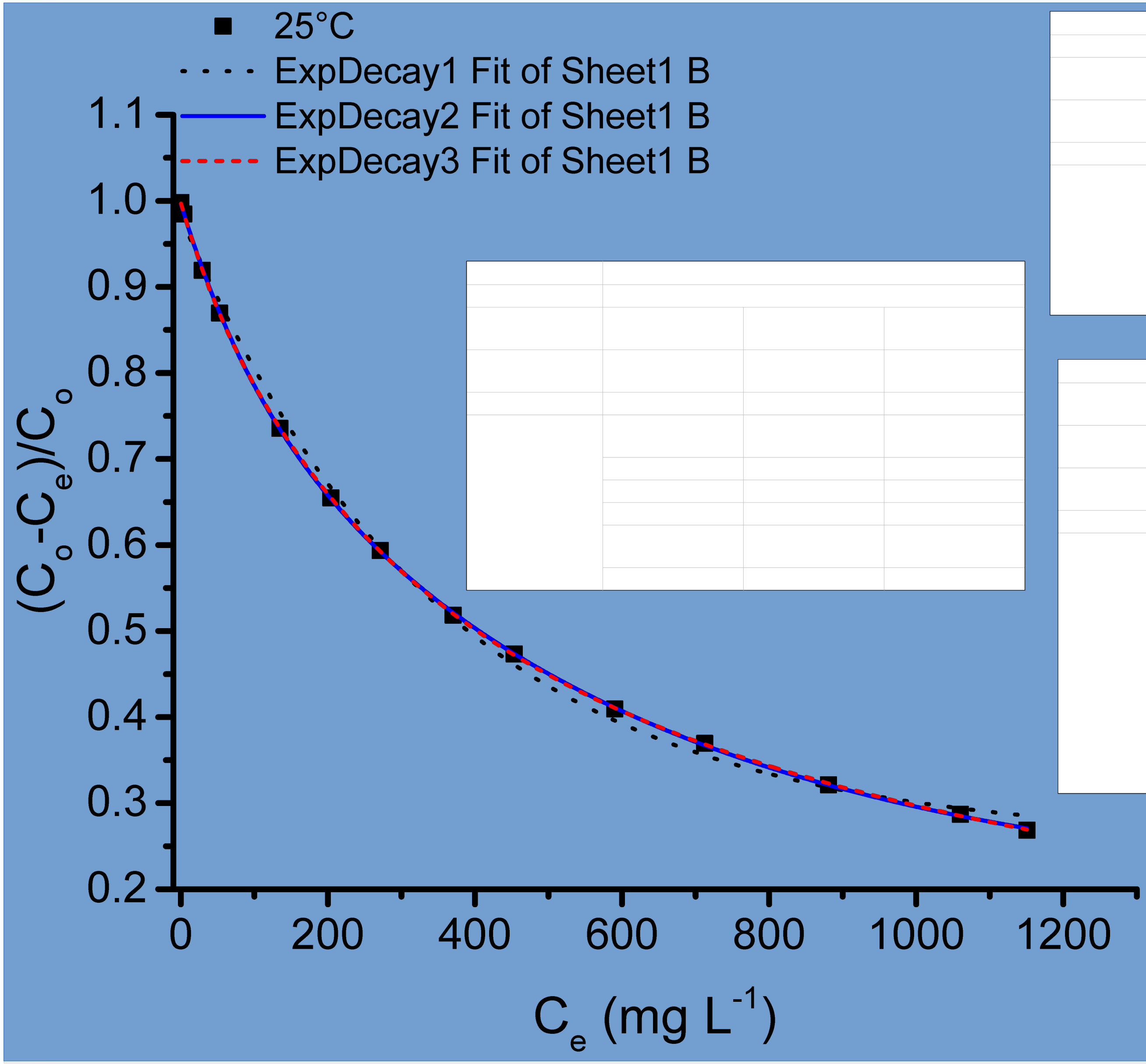



Curve after deleting 2 experimental points
Still the curve is not linear

The term $\frac{q_e}{C_e}$ *was* multiplied by $\frac{m}{V}$ in order to the ratio become dimensionless

Point	Co (mg/L					
	0					

The *“supposed equilibrium constant”* has not a fixed value



In the fitted curve

T (°C	K Liu (L/		
25	0.3		
30	0.2		

T (°C	K Liu (L/m						
25	0.35						
30	0.29						

T (°C	K Liu (L/mg						
25	0.357						
30	0.290						

$$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$$

$$\Delta G^{\circ} = -RTLn(K_e)$$

$$K_e = \frac{(1000.Kg.\text{molecular weight of adsorbate. activity coefficient of adsorbate})}{\text{unitary activity of adsorbate}}$$

$$Ln(K_e) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R} x \frac{1}{T}$$

K_g- is the best equilibrium constant obtained from isotherms (L/mg)

Activity coefficient is assumed to be 1.000

Unitary activity of adsorbate 1 mol/L

T (K)	K Liu (L/mg				
298	0.35				
303	0.29				
308	0.25				

1/T (K^{-1})	Ke					
0.003356	3.560E+05					
0.003300	2.888E+05					
0.003247	2.580E+05					
0.003195	2.175E+05					

Values of K_e obtained from

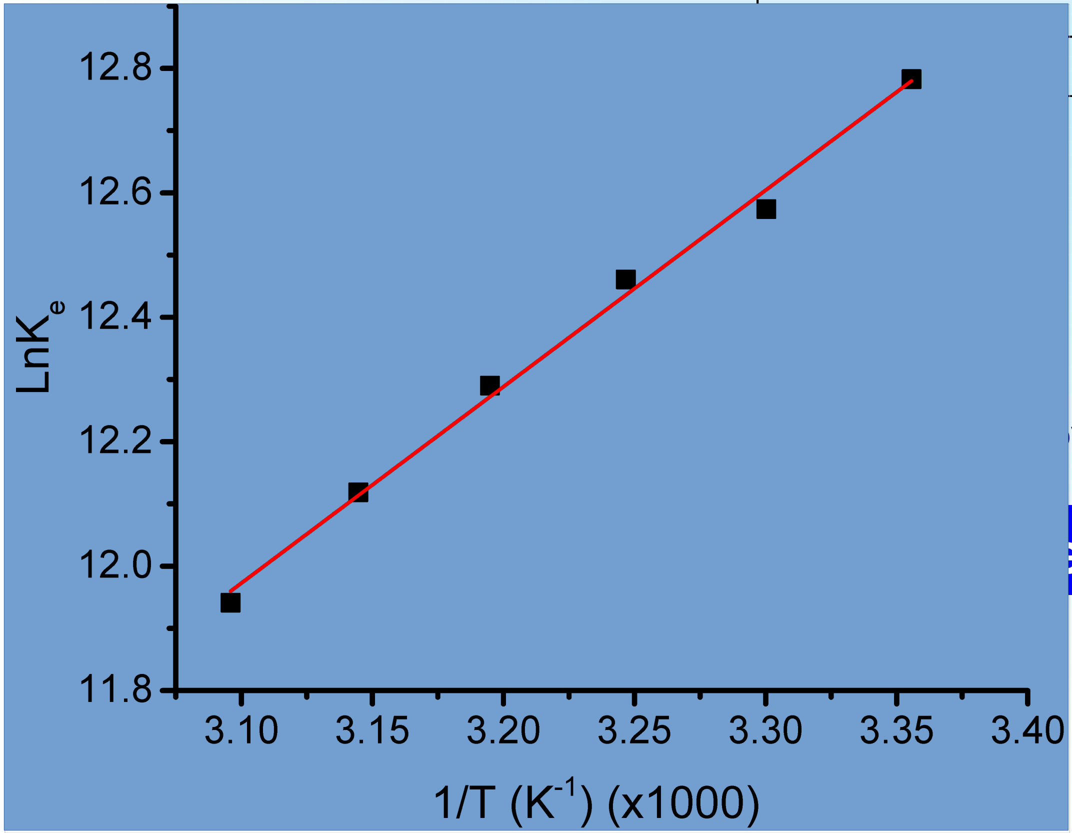
Nonlinear fitting of isotherms

Considering the best isotherm

Model that was fitted by the ex

perimental results

Constant of equilil			
Equation			
Weight			



of changes of enthalpy and changes of

y compatible with Physical adsorption

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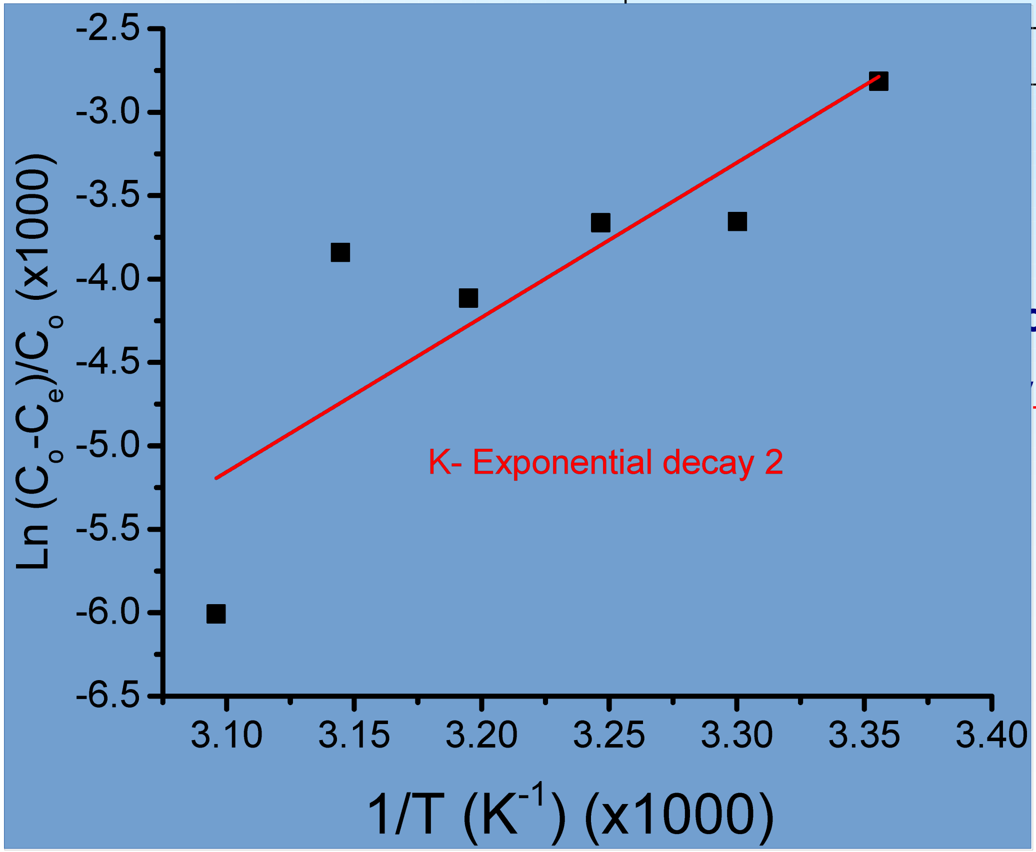
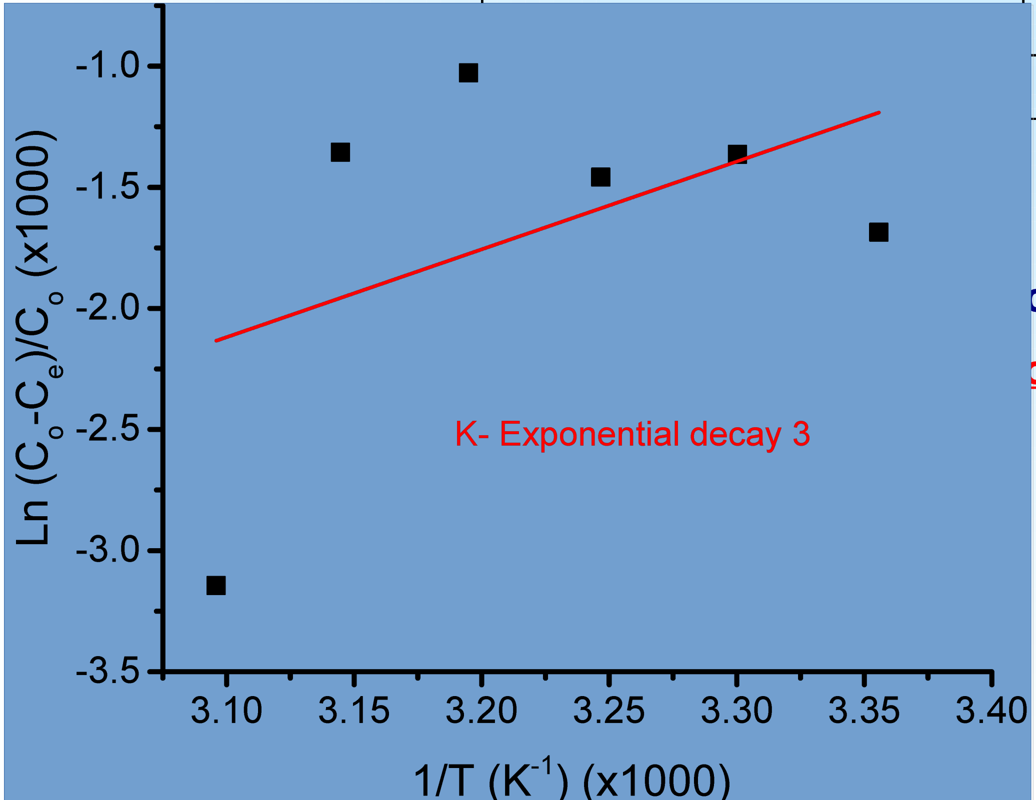
Constant of equilib			
Equation			
Weight			
Residual Sum of S			



of changes of enthalpy and changes of

not compatible with Physical adsorption

Constant of equi			
Equation			
Weight			



changes of enthalpy and changes of

ot compatible with Physical adsorption

Other Common error found throughout the Adsorption papers

$$R_L = \frac{1}{1 + K_L.C_o}$$

Mathematically R_L always will be < 1

Unless KL or Co is negative. However, initial concentration

Could not be negative, as well as the Langmuir equilibrium

Constant also, could not be negative.

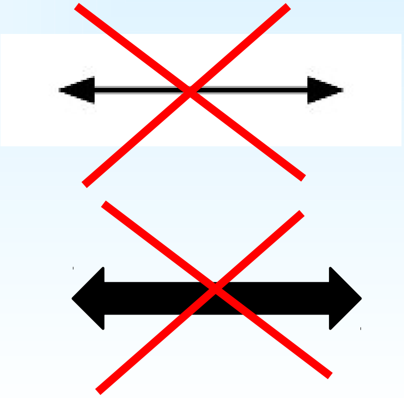
There is no sense of using this equation to affirm that the Adsorption is favorable

$$\xcancel{R_L = \frac{1}{1 + K_L . C_o}}$$

Double arrow for chemical equilibrium

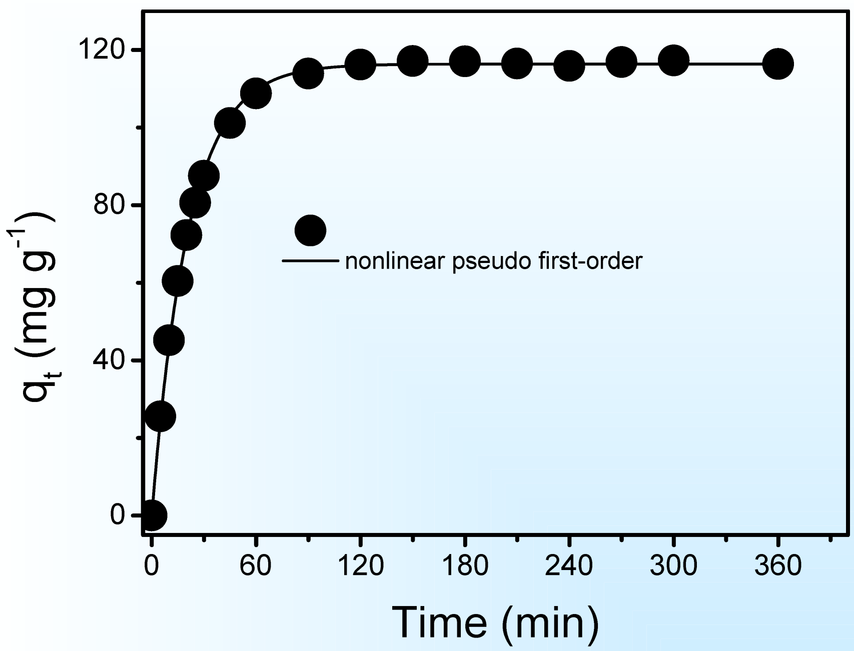
$\text{Adsorbent}_{(s)} + \text{Adsorbate}_{(aq)} \qquad \text{Adsorbent-Adsorbate}_{(s)}$

Arrow for resonance

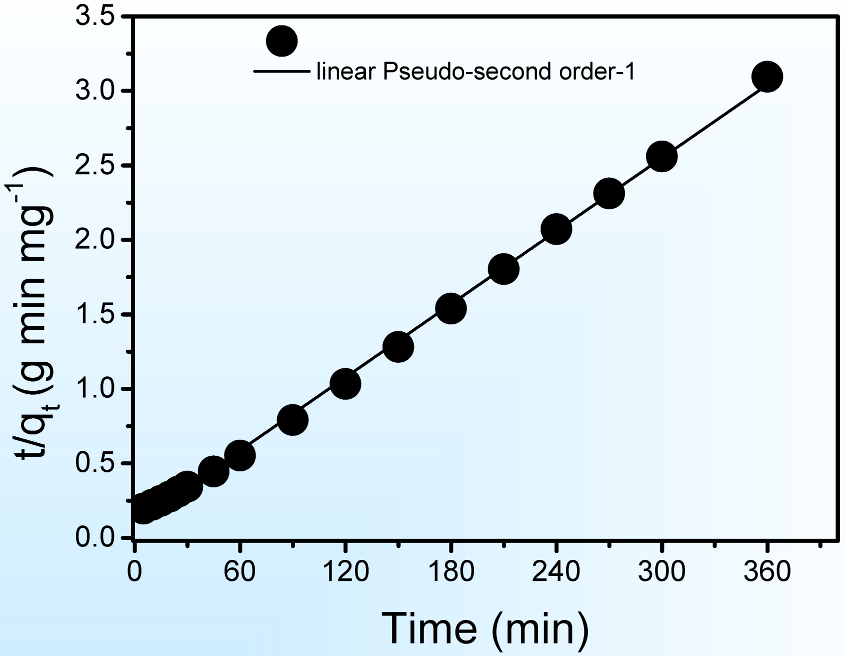


Do not use these arrows

For chemical equilibrium



Number of Points	**18**
Degrees of Freedom	**16**
Reduced Chi-Sqr	**0.703173999134**
Residual Sum of Squares	**11.2507839861**
R Value	**0.999747333076**
R-Square(COD)	**0.999494729992**
Adj. R-Square	**0.999463150616**
SD	**0.838554708492 mg/g**



Number of Points	**17**
Degrees of Freedom	**15**
Reduced Chi-Sqr	**0.00119286907145**
Resid. Sum of Sq.	**0.0178930360717**
R Value	**0.999371827709**
R-Square(COD)	**0.998744050019**
Adj. R-Square	**0.99866032002**
SD	**0.0345379366993 g min/mg**

Using linearized kinetic models the kinetics follow pseudo-second order

Using nonlinearized kinetic models, the pseudo-first model is the best choice

If one will use linearized kinetic of adsorption; you do not Need to do it, ***“All linearized kinetic adsorption models will Better fit to pseudo-second-order kinetic model”. “You even do not need to plot your results, because this is the only kinetic adsorption model that is linearized”.***

$$\xcancel{\frac{t}{q_t} = \frac{1}{k \times q_e^2} + \frac{1}{q_e} t}$$

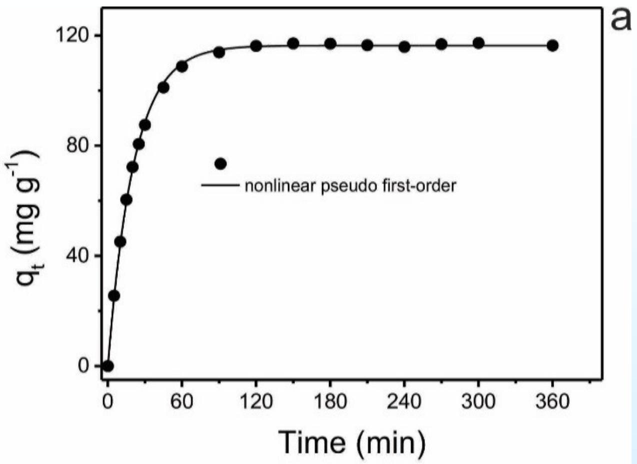
Pseudo-first order and pseudo-second-order kinetic adsorption models

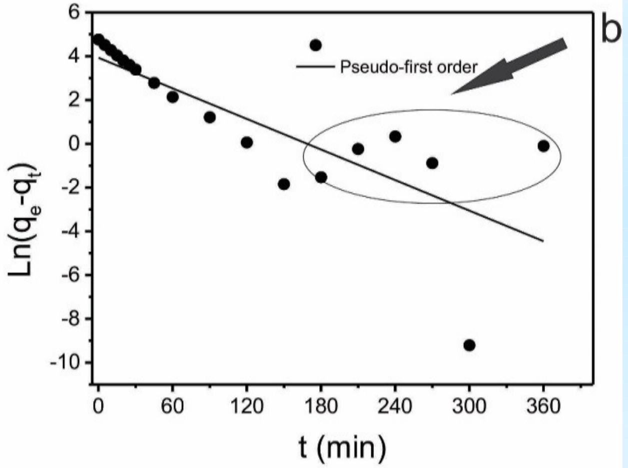
Dados de Cinética de adsorção

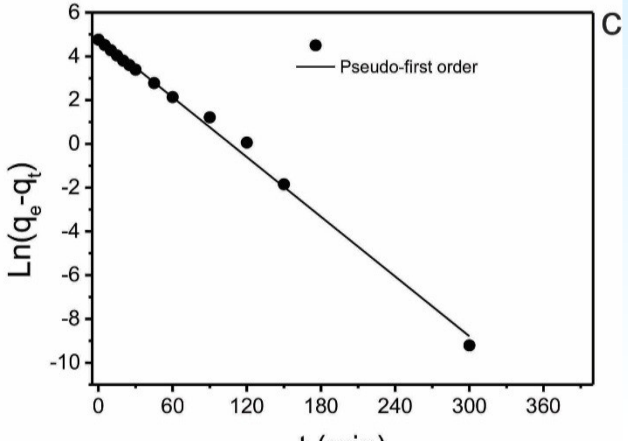
Dados experimentais

Dados manipulados

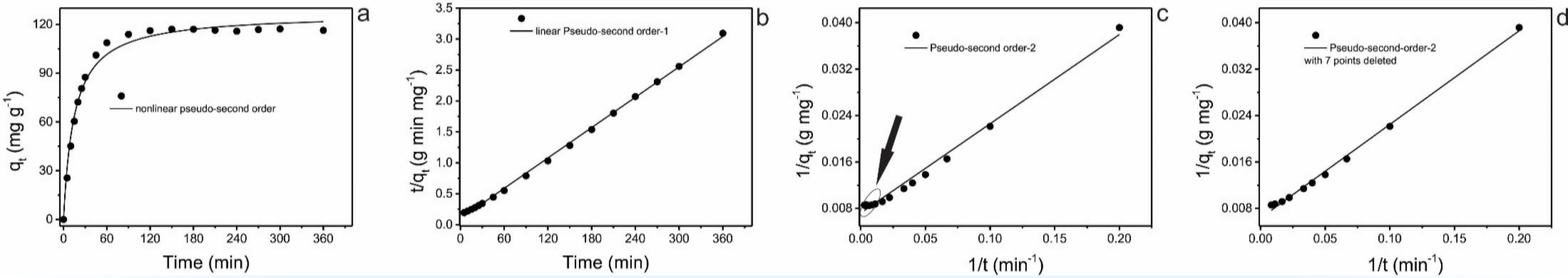
t (min)	q_t (mg g^{-1})	$Ln(q_e-q_t)$	t/q_t (min g mg^{-1})	$1/q_t$ (g mg^{-1})	1/t (min^{-1})	q_t/t (mg g^{-1} min^{-1})
0	0.0000	4.7643	-	-	-	-
5	25.5363	4.5186	0.1958	0.0392	0.2000	5.1073
10	45.1580	4.2779	0.2214	0.0221	0.1000	4.5158
15	60.4185	4.0400	0.2483	0.0166	0.0667	4.0279
20	72.2459	3.8066	0.2768	0.0138	0.0500	3.6123
25	80.5830	3.6017	0.3102	0.0124	0.0400	3.2233
30	87.5292	3.3917	0.3427	0.0114	0.0333	2.9176
45	101.1273	2.7799	0.4450	0.0099	0.0222	2.2473
60	108.7337	2.1413	0.5518	0.0092	0.0167	1.8122
90	113.8832	1.2124	0.7903	0.0088	0.0111	1.2654
120	116.1828	0.0600	1.0329	0.0086	0.0083	0.9682
150	117.0870	-1.8477	1.2811	0.0085	0.0067	0.7806
180	117.0279	-1.5292	1.5381	0.0085	0.0056	0.6502
210	116.4573	-0.2391	1.8032	0.0086	0.0048	0.5546
240	115.8487	0.3335	2.0717	0.0086	0.0042	0.4827
270	116.8314	-0.8838	2.3110	0.0086	0.0037	0.4327
300	117.2445	-9.2103	2.5588	0.0085	0.0033	0.3908
360	116.3430	-0.1036	3.0943	0.0086	0.0028	0.3232



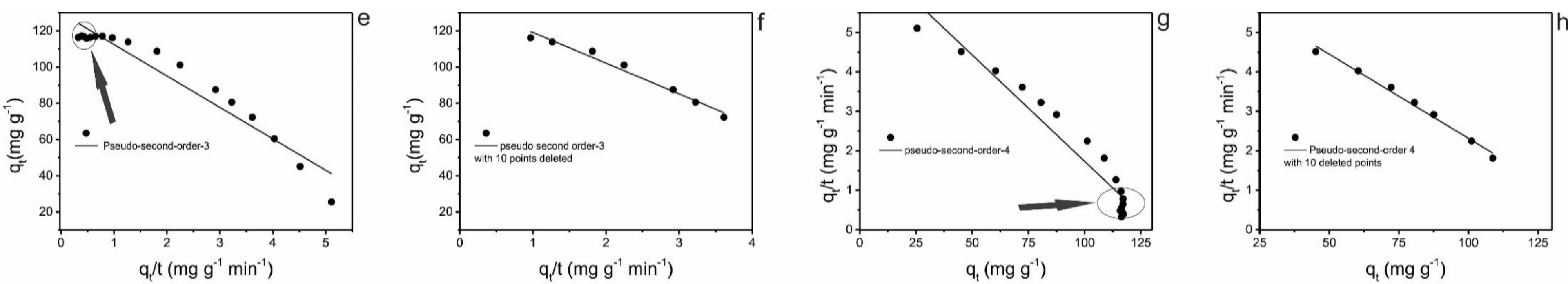




Parameter	value
Nonlinear pseudo-first order	(a)
k_1 (min^{-1})	0.04766
q_e (mg g^{-1})	116.4
Number of Points	18
Degrees of Freedom	16
Reduced Chi-Sqr (mg g^{-1})	0.7032
Residual Sum of Squ.(mg g^{-1})^2	11.25
R Value	0.9997
R-Square(COD)	0.9995
Adj. R-Square	0.9995
SD (mg g^{-1})	0.8386
Pseudo-first order-1	(b)
k_1 (min^{-1})	0.02329
q_e (mg g^{-1})	50.83
Number of Points	18
Degrees of Freedom	16
Reduced Chi-Sqr (min g mg^{-1})	4.621
Resid. Sum of Sq.(min g mg^{-1})^2	73.94
R Value	0.7907
R-Square(COD)	0.6252
Adj. R-Square	0.6018
SD (min g mg^{-1})	2.150
Linear pseudo-first order-2	(c)
k_1 (min^{-1})	0.04549
q_e (mg g^{-1})	128.3
Number of Points	13
Degrees of Freedom	11
Reduced Chi-Sqr (min g mg^{-1})	0.08455
Residual Sum of Squ. (min g mg^{-1})^2	0.9301
R Value	0.9974
R-Square(COD)	0.9947
Adj. R-Square	0.9942
SD (min g mg^{-1})	0.2908

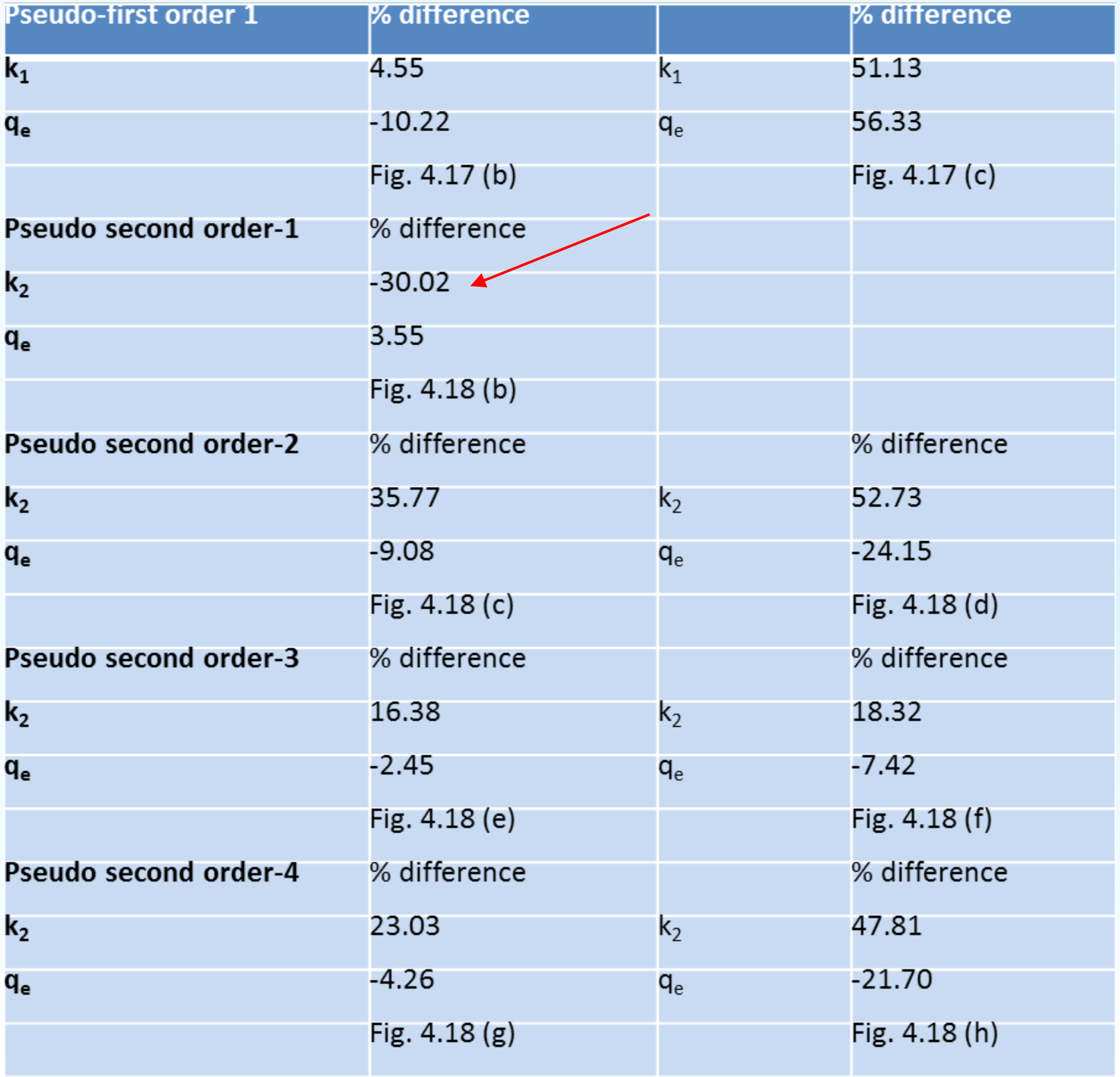


Parameter	value	Parameter	value
Nonlinear pseudo-second order	Fig. 4.18 (a)	Linear Pseudo-second order-1	Fig. 4.18 (b)
k_2 (min g mg^{-1})	$5.306.10^{-4}$	k_2 (min g mg^{-1})	$6.899.10^{-4}$
q_e (mg g^{-1})	126.7	q_e (mg g^{-1})	122.2
Number of Points	18	Number of Points	17
Degrees of Freedom	16	Degrees of Freedom	15
Reduced Chi-Sqr (mg g^{-1})	18.02	Red. Chi-Sqr (min g mg^{-1})	0.001193
Res Sum of Squ.(mg g^{-1})^2	288.2	Res.Sum of Squ(min g mg^{-1})^2	0.01789
R Value (COC)	0.9935	R Value (COC)	0.9994
R-Square(COD)	0.9871	R-Square(COD)	0.9987
Adj. R-Square	0.9862	Adj. R-Square	0.9987
SD (mg g^{-1})	4.244	SD (min g mg^{-1})	0.03454
Linear pseudo-second order-2	**Fig. 4.18 (c)**	**Linear pseudo-second order-2**	**Fig. 4.18 (d)**
k_2 (min g mg^{-1})	$3.408.10^{-4}$	k_2 (min g mg^{-1})	2.508E-04
q_e (mg g^{-1})	138.2	q_e (mg g^{-1})	157.3
Number of Points	17	Number of Points	10
Degrees of Freedom	15	Degrees of Freedom	8
Reduced Chi-Sqr (g mg^{-1})	$6.490.10^{-7}$	Reduced Chi-Sqr (g mg^{-1})	$3.203.10^{-7}$
Res.l Sum of Squ.(g mg^{-1})^2	$9.735.10^{-6}$	Res. Sum of Squ.(g mg^{-1})^2	$2.562.10^{-6}$
R Value (COC)	0.9950	R Value (COC)	0.9984
R-Square(COD)	0.9900	R-Square(COD)	0.9968
Adj. R-Square	0.9894	Adj. R-Square	0.9964
SD (g mg^{-1})	$8.056.10^{-4}$	SD (g mg^{-1})	$5.659.10^{-4}$



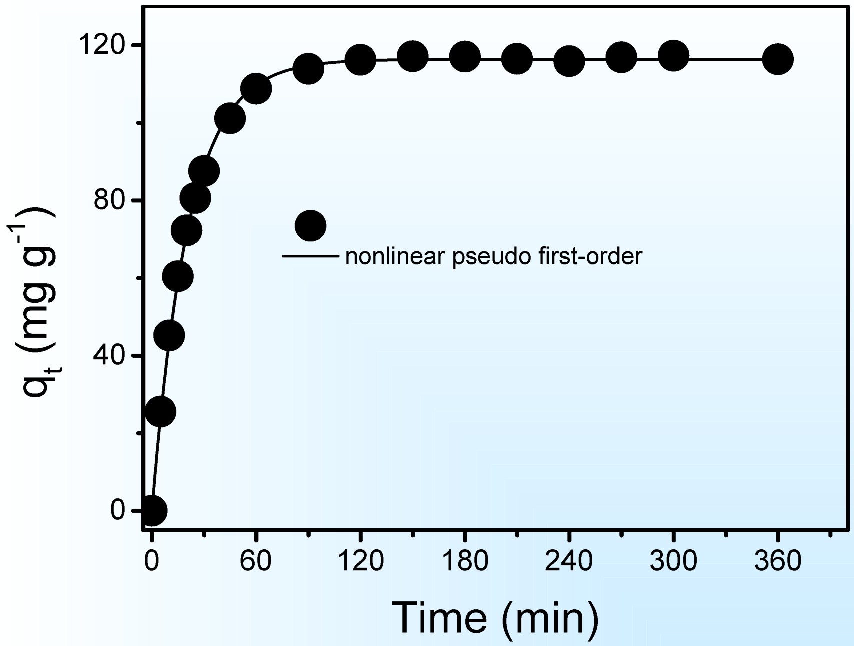
Linear pseudo-second order-3	Fig. 4.18 (e)	Linear pseudo-second order-3	Fig. 4.18 (f)
k_2 (min g mg^{-1})	4.437.10^{-4}	k_2 (min g mg^{-1})	4.334.10^{-4}
q_e (mg g^{-1})	129.8	q_e (mg g^{-1})	136.1
Number of Points	17	Number of Points	7
Degrees of Freedom	15	Degrees of Freedom	5
Reduced Chi-Sqr (mg g^{-1})	57.27	Reduced Chi-Sqr (mg g^{-1})	8.453
Residual Sum of Squ.(mg g^{-1})^2	859.1	Residual Sum of Squ.(mg g^{-1})^2	42.27
R Value	0.9679	R Value	0.9881
R-Square(COD)	0.9368	R-Square(COD)	0.9762
Adj. R-Square	0.9326	Adj. R-Square	0.9715
SD (mg g^{-1})	7.568	SD (mg g^{-1})	2.907
Linear pseudo-second order-4	**Fig. 4.18 (g)**	**Linear pseudo-second order-4**	**Fig. 4.18 (h)**
k_2 (min g mg^{-1})	4.084.10^{-4}	k_2 (min g mg^{-1})	2.769.10^{-4}
q_e (mg g^{-1})	132.1	q_e (mg g^{-1})	154.2
Number of Points	17	Number of Points	7
Degrees of Freedom	15	Degrees of Freedom	5
Reduced Chi-Sqr .(mg g^{-1}min^{-1})	0.1780	Reduced Chi-Sqr .(mg g^{-1}min^{-1})	0.01228
Res. Sum of Squ.(mg g^{-1}min^{-1})^2	2.669	Resid. Sum of Squ(mg g^{-1}min^{-1})^2	0.06140
R Value	0.9679	R Value	0.9944
R-Square(COD)	0.9368	R-Square(COD)	0.9888
Adj. R-Square	0.9326	Adj. R-Square	0.9866
SD (mg g^{-1}min^{-1})	0.4218	SD.(mg g^{-1}min^{-1})	0.1108

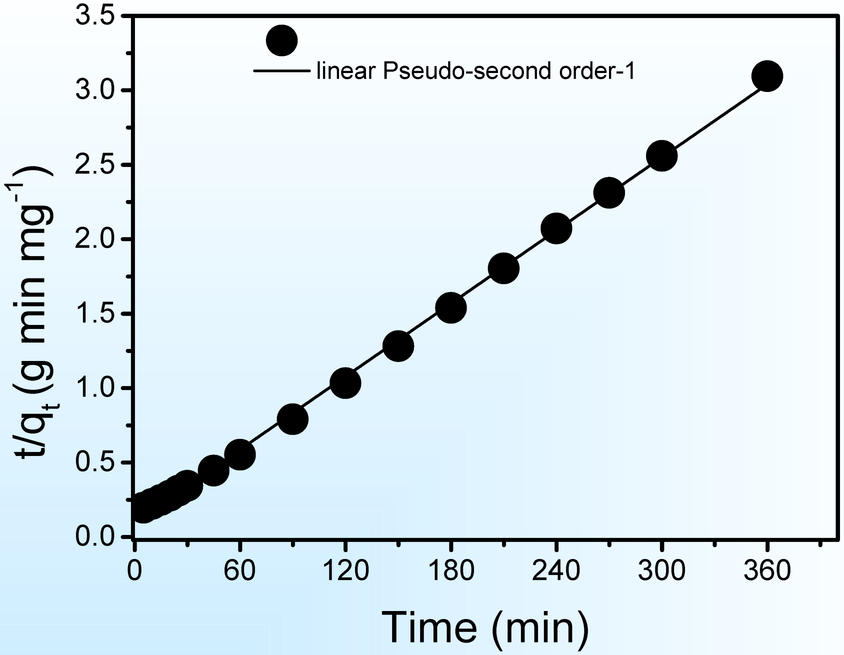
Table 3.10. Relative differences of q_e and *k1* or *k2* kinetic parameters of linearized pseudo-first order, linearized pseudo-second order-1, linearized pseudo-second order-2, pseudo-second order-3 and pseudo-second order-4 in relation to nonlinear pseudo-first order and nonlinear pseudo-second order equations. Values are expressed in percentage.



Pseudo-first order 1	% difference		% difference
k_1	4.55	k_1	51.13
q_e	-10.22	q_e	56.33
	Fig. 4.17 (b)		Fig. 4.17 (c)
Pseudo second order-1	% difference		
k_2	-30.02		
q_e	3.55		
	Fig. 4.18 (b)		
Pseudo second order-2	% difference		% difference
k_2	35.77	k_2	52.73
q_e	-9.08	q_e	-24.15
	Fig. 4.18 (c)		Fig. 4.18 (d)
Pseudo second order-3	% difference		% difference
k_2	16.38	k_2	18.32
q_e	-2.45	q_e	-7.42
	Fig. 4.18 (e)		Fig. 4.18 (f)
Pseudo second order-4	% difference		% difference
k_2	23.03	k_2	47.81
q_e	-4.26	q_e	-21.70
	Fig. 4.18 (g)		Fig. 4.18 (h)

$$\ln k_{kinetic} = \ln A - \frac{E_a}{RT}$$





Number of Points 18
Degrees of Freedom 16
Reduced Chi-Sqr 0.703173999134
Residual Sum of Squares 11.2507839861
R Value 0.999747333076
R-Square(COD) 0.999494729992
Adj. R-Square 0.999463150616
SD 0.838554708492 mg/g

Number of Points 17
Degrees of Freedom 15
Reduced Chi-Sqr 0.00119286907145
Resid. Sum of Sq. 0.0178930360717
R Value 0.999371827709
R-Square(COD) 0.998744050019
Adj. R-Square 0.99866032002
SD 0.0345379366993 g min/mg

Using linearized kinetic models the kinetics follow pseudo-second order

Using nonlinearized kinetic models, the pseudo-first model is the best choice

If one will use linearized kinetic of adsorption; you do not Need to do it, “*All linearized kinetic adsorption models will Better fit to pseudo-second-order kinetic model”. “You even do not need to plot your results, because this is the only kinetic adsorption model that is linearized”.*

$$\xcancel{\frac{t}{q_t} = \frac{1}{k \times q_e^2} + \frac{1}{q_e} t}$$

$$\xcancel{\frac{t}{q_t} = \frac{1}{k \times q_e^2} + \frac{1}{q_e} t}$$

~~If the kinetic data follow the pseudo-second order, the Mechanism of adsorption will be chemisorption~~

Majority of adsorption process are physio-sorption and not Chemisorption.

Chemisorpton would the complexation of metallic ions by ligands

Organic molecules will predominate – physical adsorption.

If you do not agree, provide a XPS, proving that an chemical Bond was formed, after the adsorption of organic molecule Over the surface of an adsorbent.

Kinetic adsorption models are not absolute, the mechanism of adsorption should be verified by several and different Analytical techniques.

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Comments on the paper: a critical review of the applicability of Avrami fractional kinetic equation in adsorption-based water treatment studies

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ABSTRACT

This letter presents comments on the paper "Critical review on the applicability of Avrami fractional kinetic equation in adsorption-based water treatment studies" that was recently published in Desalination and Water Treatment by N.A. Oladoja. This author explained the misuse of Avrami-type kinetic equation in adsorption process at solid/solution interfaces and also mentioned few of the papers published in the literature that used the Avrami kinetic equation. We, therefore, decided to write this letter to make it clearer to the reader that there are no wrong or unfounded concepts in the papers cited in the review of N.A. Oladoja. We do believe that the mechanism of adsorption could only be established by several analytical techniques and a good sense of chemistry associated with the equilibrium and kinetic data. The mechanism cannot be directly assigned based on just simple kinetic experiments. In addition, the author was very selective in choosing some specific papers, which used this valuable kinetic adsorption equation, for his criticism. The kinetic equation presented at the end of Oladoja's paper is worthless and may not be a feasible equation that can be applied to adsorption from solutions.

Keywords: Avrami fractional kinetic adsorption model; Kinetics of adsorption; Interpretation of Avrami equation

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E.C. Lima, M.A. Adebayo, F. M. Machado, Chapter 3- Kinetic and Equilibrium Models of Adsorption in Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications, C.P. Bergmann, F.M. Machado editors, ISBN 978-3-319-18874-4, Springer 2015, pp.33-69. DOI 10.1007/978-3-319-18875-1_3.

Link for the Chapter 3 as well as Physical Chemistry Book.

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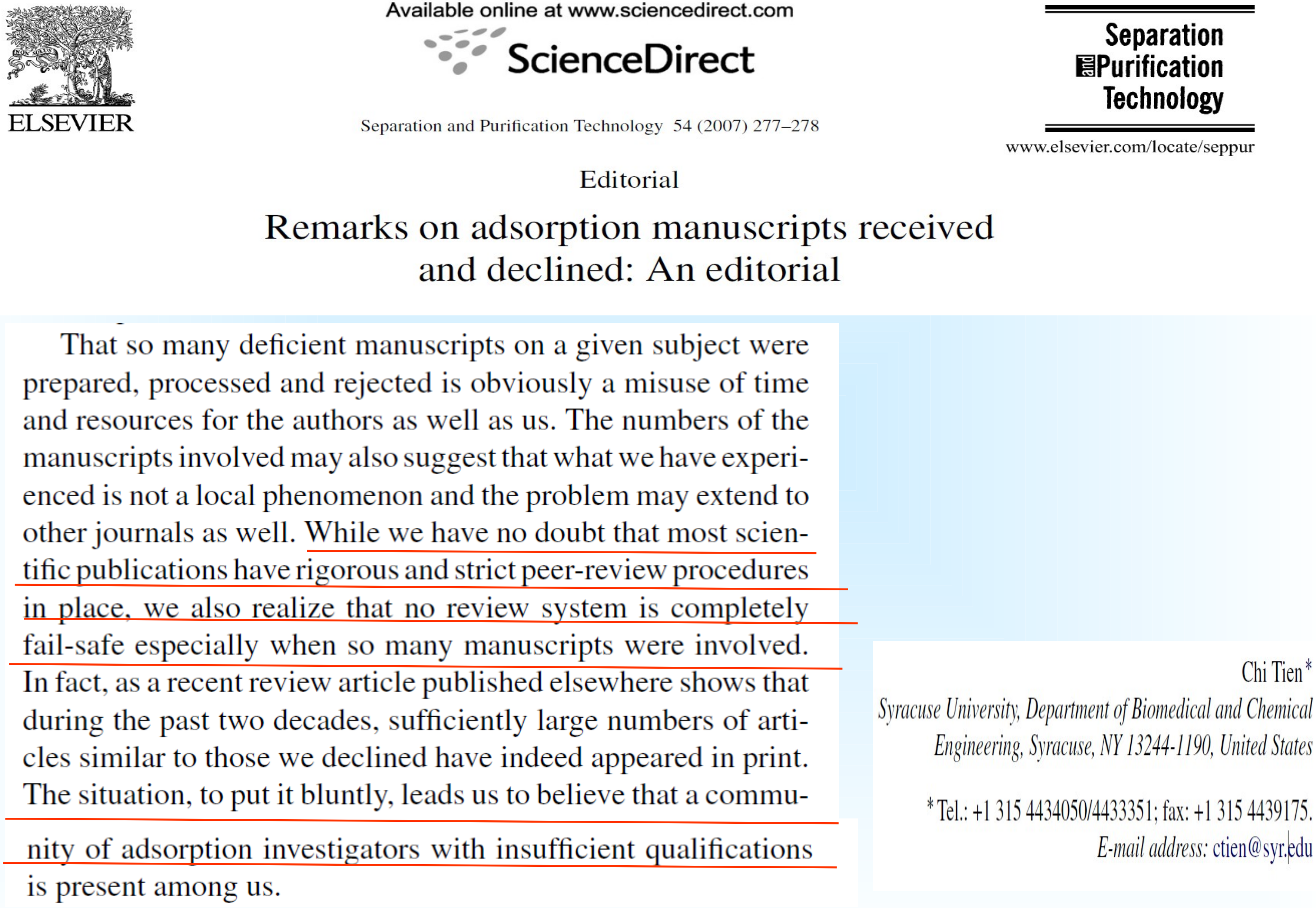

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Editorial

Remarks on adsorption manuscripts received and declined: An editorial

That so many deficient manuscripts on a given subject were prepared, processed and rejected is obviously a misuse of time and resources for the authors as well as us. The numbers of the manuscripts involved may also suggest that what we have experienced is not a local phenomenon and the problem may extend to other journals as well. While we have no doubt that most scientific publications have rigorous and strict peer-review procedures in place, we also realize that no review system is completely fail-safe especially when so many manuscripts were involved. In fact, as a recent review article published elsewhere shows that during the past two decades, sufficiently large numbers of articles similar to those we declined have indeed appeared in print. The situation, to put it bluntly, leads us to believe that a community of adsorption investigators with insufficient qualifications is present among us.

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Thank you for your special attention