

Correlation of the equilibrium sorption of crude oil by expanded perlite using different adsorption isotherms at 298.15 k

A. Alihosseini^{1,*}, V. Taghikhani², A.A.Safekordi² and D.Bastani²

¹Department of Chemical, Islamic Azad University, Ilam Campus, Ilam, Iran.

²Department of Chemical and petroleum Engineering, Sharif University of Technology, Tehran, Iran.

Abstract

In this work the recently published experimental data on the sorption capacity of expanded perlite to crude oil were correlated with the equilibrium isotherm of Langmuir, Freundlich, Tempkin and the three parameter Redlich-Peterson isotherms. The results obtained from each specified isotherms were compared and accuracy of the models were favorably discussed. Accuracy of each model was obtaining function. The effect of type of objective function on the final results was investigated. To bring up the idea the ERAV, ERRSQ, HYBRID, MPSD and Chi-Square objective function were used and the accuracy obtained using each objective function. The results showed the Redlich-Peterson model can better represent the equilibrium isotherm data for the crude oil to be up taken on the expanded perlite.

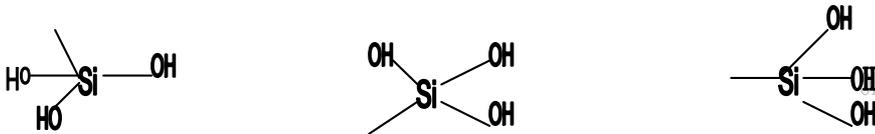
Keyword: Expanded perlite, Sorption capacity, adsorption isotherms

Corresponding author

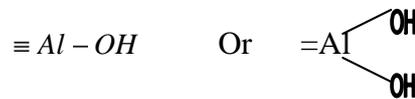
Introduction

Sorption techniques produce high-quality treated effluents and sorption processes have been investigated as method of removing crude oil from seawater [1]. Exfoliated graphite and activated carbon are high effective for the removal of spill oil from seawater [2]. However, the use of exfoliated graphite and activated carbon may not be suitable in developing countries because of its high cost. Thus, it is more suitable to use adsorbents such as clay minerals, peat and wood powder [3-5]

Among them clay minerals such as perlite has received great deal of attention. Perlite has a low density, high surface area, and a low thermal conductivity. Also since most perlite samples have high silica content (usually greater than 70%), they are high privileged with adsorptive characteristics [6]. The adsorptive character of perlite is due to the silanol groups, which are formed by silicon atoms on the surface of perlite [7]. The types of silanol groups are shown as follows:



The hydrous oxide surface groups in alumina are given as follows (Bilal.Acemioglu, 2004).



The silicon atoms at the surface tend to maintain their tetrahedral coordination with oxygen. They complete their coordination at room temperature by attachment to monovalent hydroxyl groups, forming silanol groups. The surface of perlite becomes more negatively or positively charged according to the pH of the medium. This situation affects sorption capacity.

Also expanded perlite is an inert chemical that can be used as excellent filter aid and as filler in various processes and materials [8]. Moreover, expanded perlite is commonly used in the processing of vegetable fat, juice, beer in food industry. It is also used in cleaning of dams and ponds in aquatic environment, in obtaining of a clear liquid as a filter product, growing of seed and regularizing of the soil in agriculture and in so many other industrial applications.

Adsorption has been an effective separation process for a wide variety of applications. The most widely used adsorbent for industrial applications is exfoliated graphite and activated carbon. The analysis of the isotherm data is important to develop an analytic equation which accurately represents the results and could be used for design purposes. The most well-known isotherms applied in solid-liquid systems are the theoretical equilibrium isotherm. Freundlich, the earliest known relationship describing the earlier presented, Langmuir the best known and most often used isotherm for sorption of solute from a liquid solution. Redlich-peterson containing three parameters isotherm, this equation is combining of Freundlich and Langmuir isotherms And Tempkin is isotherm that representation for data equilibrium of adsorption [9-12].

Linear regression was frequently used to determine the most fitted model throughout the years and the method of least square has been frequently used for finding the parameters of the models. However, transformations of non-linear isotherm equations to linear form implicitly alter their error structure and may also violate the error variance and normality assumption of standard least squares.

In this study, a comparison of linear regression and five different error functions as: a) the sum of square of the average squares of the errors (ERAV). b) The sum of the squares of the errors (ERRSQ). C) The hybrid fractional error function (HYBRID). d) Marquardt's percent standard deviation (MPSD). e) Chi-square analysis, (χ^2). Were examined of four isotherms, Langmuir,

Freundlich, Redlich-Peterson and Tempkin and have been applied to the experiment of

crud oil sorption on expanded perlite [13-14].

In this work, cost-effective expanded perlite samples were selected as a sorbent for the investigation of sorption isotherm of crude oil from oil and seawater mixing. Perlite is glass volcanic rock varying in color from gray to black. When it is heated to elevated temperatures (850-1100° c), it expands to 35 times its internal volume, and it is named 'expanded perlite' [15].

Theory

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption equilibrium is the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm. There are many theories relating to adsorption equilibrium.

Langmuir isotherm

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. Graphically, plateau characterizes the Langmuir isotherm. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Sorption is assumed to take place at that site. In Eq. (2), K_L and a_L are the Langmuir isotherm constants while C_e is the oil weight in the liquid phase and q_e is the oil weight in the solid phase at equilibrium.

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

The Langmuir constant, K_L and a_L are evaluated of the linearization of Eq.2. The linear expression takes the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (3)$$

Hence by plotting C_e/q_e against C_e it is possible to obtain the value of K_L from the intercept that is $(1/K_L)$ and the value of a_L from the slope, which is (a_L/K_L) . The theoretical monolayer capacity is Q_0 and is numerically equal to (K_L/a_L) . The Langmuir equation is applicable to homogeneous sorption where the sorption of each molecule has equal sorption activation energy. The equation is thermodynamically consistent and follows Henry's Law at low concentrations. Therefore as C_e becomes lower, $a_L C_e$ is much less than unity and q_e , that is, analogous to Henry's Law.

Freundlich isotherm

The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases with the concentration of adsorbate on the adsorbent surface. Theoretical, using this expression, an infinite amount of adsorption can occur.

$$q_e = K_F C_e^{b_f} \quad (4)$$

In this equation K_F and b_f are the Freundlich constants. This expression is characterized by the heterogeneity factor, b_f , and thus the Freundlich isotherm may be used to describe heterogeneous system [16-17]. The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's Law) at Low surface coverage. Both these theories suffer from a drawback that equilibrium data over a wide concentration range cannot be fitted with a single set of constants. To determine the constant K_f and b_f , the linear form of the equation as shown below may be used to plot $\ln(q_e)$ against $\ln(C_e)$ as:

$$\ln q_e = \ln K_f + b_f \ln C_e \quad (5)$$

Redlich - Petertson isotherm

Redlich and Peterson proposed an empirical three parameter equation which may be used to represent adsorption equilibrium over a wide concentration range of adsorbate. The adsorbate concentration at equilibrium condition can be computed as follows

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (6)$$

Where β is a constant parameter and is normally less than unity. This equation reduces to a linear isotherm at low surface coverage. As a matter of fact it turns to the Freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when β is set to be unity. However, the equation cannot be linearised for easy estimation of the isotherm parameter K_R , a_R and β . The linearization of the expression gives the following relation:

$$\frac{C_e}{q_e} = \frac{1}{K_R} + \frac{a_R}{K_R} C_e^\beta \quad (7)$$

Plotting C_e/q_e against C_e^β yields a straight line with slope = $\frac{a_R}{K_R}$ and intercept = $\frac{1}{K_R}$. However,

plotting of Eq. (7) is not applicable because of three unknown parameters contained within the equation. Therefore, a minimization procedure is adopted to maximize the correlation coefficient between the theoretical data for q_e predicted from Eq. (7) and the corresponding experimental data. More often, the method used to determine isotherm parameters is the linear regression with transformed variables. The quality of the fit of the experimental data with the isotherm equation is assessed on the magnitude of the correlation coefficient for the regression. In other words, the isotherm giving the correlation coefficient closest to unity provides the best fit.

Tempkin isotherm

Tempkin and pyzhev considered the effect of some indirect adsorbate/adsorbate interaction on adsorption isotherms and suggested that because of interaction the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The amount of adsorbate can be given as below:

$$q_e = \left(\frac{RT}{b} \right) \ln AC_e \quad (8)$$

Eq. (8) can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \quad (9)$$

With

$$B = \frac{RT}{b} \quad (10)$$

The adsorption data can be analyzed according to Eq. (9) and a plot of q_e versus $\ln C_e$ enables the determination of the isotherm constant, A and B, It would be worth noting that the constant B is related to heat of adsorption.

Error functions

In the context of the current work, five different error functions were examined and in each case the respective error function across the liquid phase concentration range using the QBasic software.

1. The sum of square of the average squares of the errors (ERAV). Here, the error function minimized the fractional error distribution across the entire concentration range

$$ERAV = \left[\frac{1}{p} \sum_{i=1}^p (q_{e,calc} - q_{e,meas})^2 \right]^{1/2} \quad (11)$$

Where $q_{e,calc}$ equilibrium capacity obtained by calculated from model (mg/g) and $q_{e,meas}$ was the equilibrium capacity (mg/g) from the experimental data. If data from the model are similar to the experimental data, ERAV will be a small number; if they are different, ERAV will be a large number [18].

2. The sum of the squares of the errors (ERRSQ): This widely used error function has one major drawback. The function will result in the calculated isotherm parameters providing a better fit at the higher end of the liquid phase concentration range. This is because the magnitude of the errors and hence the square of the errors will increase as concentration increases.

$$ERRSQ = \sum_{i=1}^p (q_{e,calc} - q_{e,meas})_i^2 \quad (12)$$

3. The hybrid fractional error function (HYBRID): This error function was developed in order to improve the fit of the ERRSQ method at low concentration values. In this method each ERRSQ value was divided by the experimental solid phase concentration q value. In addition a divisor was included as a term for the number of degrees of freedom for the system, the number of data points minus the number of parameters within the isotherm equation.

$$HYBRID = \frac{100}{P-n} \sum_{i=1}^p \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right] \quad (13)$$

4. Marquardt's percent standard deviation (MPSD): This error function was similar to a geometric mean error distribution which was modified to allow for the number of degrees of freedom of the system.

$$MPSD = 100 \left(\sqrt{\left(\frac{1}{p-n} \sum_{i=1}^p \left[\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right] \right)} \right) \quad (14)$$

5. Chi-square analysis, (χ^2) the advantage of using chi-square test was comparing all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was

$$\chi^2 = \sum_{i=1}^p \left(\frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,calc}} \right) \quad (15)$$

If data from model were similar to the experimental data, χ^2 would be a small number and vice versa the values of χ^2 of each model were shown in table.

Result and discussion

Table 1 presents the values of the parameters introduced by the Langmuir isotherm, i.e., a_L and k_L , associated with the correlation coefficient obtained from least square fit of the model to the corresponding experimental data [15]. Also it can be seen from table 1 that the type of objective function used to obtain the regressed values of the parameters was mentioned to be error functions. As expounded earlier the error functions can be given by equations (11-15). The Langmuir isotherm plots for sorption of crude oils on expanded perlite are presented in Fig.1. The values of the parameters can be directly used to obtain the amount of adsorbate to be sorbed onto the expanded

Perlite studied in this work. AS observed from table 1 the correlation of the Langmuir isotherm was performed with the sorption experimental data of different types of crude oil onto the expanded perlite.

Table 2 presents the values of the parameters introduced by the Freundlich isotherm, i.e., K_F and b_f , associated with the correlation coefficient obtained from least square fit of the model to the corresponding experimental data. Also it can be seen from table 2 that the type of objective function used to obtain the regressed values of the parameters was mentioned to be error functions. As expounded earlier the error functions can be given by equations (11-15). The values of the parameters can be directly used to obtain the amount of adsorbate to be sorbed onto the expanded perlite studied in this work. The Freundlich isotherm plots for sorption of crude oils on expanded perlite are presented in Fig.2. AS observed from table 2 and fig 2 the correlation of the Freundlich isotherm was performed with the sorption experimental data of different types of crude oil onto the expanded perlite.

The Redlich-peterson isotherm plots for sorption of crude oils on expanded perlite are presented in Fig.3. Again, examination of the plot shows that the Redlich-peterson isotherm accurately describes the sorption behaviors of crude oil on expanded perlite over the concentration ranges studied. The Redlich-peterson isotherm constants, K_R , a_R , β , and R^2 and errors function are presented in Table.3. Since the method used to derive the isotherm parameters maximizes the linear coefficient of determination, it is unsurprising that in this case, the Redlich-peterson isotherm exhibit extremely high R^2 values indicating, superficially at least, that it produces a considerably better fit compared to the preceding two-parameter isotherms. This equation reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when $\beta=1$

The Tempkin isotherm plots for sorption of crude oils on expanded perlite are presented in Fig.4. The Tempkin isotherm constants, A, B, R^2 and errors function are presented in Table.4.

AS observed from table 4 and fig 4 the correlation of the Tempkin isotherm was performed with the sorption experimental data of different types of crude oil onto the expanded perlite.

Conclusion

The equilibrium adsorption of two-type crude oil by expanded perlite has been reported. The results revealed the potential of the expanded perlite is suitable to be a low-cost sorbent for clean-up crude oil. The equilibrium results have been modeled and evaluated using four different isotherms and five different error functions including a linear transform model. The results showed that the equilibrium data for all the crude oil-sorbent systems fitted the Redlich-Peterson and Freundlich isotherms model best. The linear transform model provided highest correlation coefficient for the case of the Redlich-Peterson isotherm ($R^2=0.999$). The R^2 for Langmuir isotherm is 0.9132 troughs 0.93561. And the sum of square of the average squares of the errors (ERAV) equal 2.36451 for Langmuir isotherm. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Using of the error functions for optimization showed that often the isotherms were generally better represented using the ERRSQ, HYBRID and Chi-Square errors function.

References

1. Ho, Yuh. Shan. Tachiu, Wen. Wang, Chung-Chi., "Regression analysis for the sorption isotherms of basic dyes on sugarcane dust" *Bio resource Technology*. 2005; 96: 1258-1291.
2. Ingaki, Michio, Toyada, Masahiro., Iwashita, Norio, Nishi, Yoko., "Exfoliated graphite for spilled heavy oil recovery". *Carbon science*. 2001; 2: 1-8

3. Alihosseini, A., Bastani, D., Safekordi, A. A., Emulsion and Sorption Oil Spills by Expanded Perlite, *J. Env. Sci.* 2005; 23: 55-68
4. McKay, G., Ho, Y. S., "Sorption of dye from aqueous solution by peat", *Chem. Eng. J.* 1998; 70: 15-124.
5. Ghalambor. Ali, "Composting technology for practical and safe remediation of oil spill residuals" technical report series. 1999; 98-00
6. Dogan, M., Alkan, M., Onganer, Y., "Adsorption of methylene blue from aqueous solution onto perlite" *Water Air Soil Pollute.* 2000; 120:229-248
7. Acemioglu, Bilal., "Batch kinetic study of sorption of methylene blue by perlite" *Chem.Eng.J.* 2005; 106: 73-81
8. Polatli, M., Erdinc, M., Erdinc, E., Okayay, E., "Perlite exposure and 4-years change in lung function" *Environ.Res.Sec.* 2001; 86:238-243
9. Freundlich, H., "Adsorption in solution" *Phys. Chemise.* 1906; 57: 384-410
10. Langmuir, I., "Adsorption of gases on plane surfaces of glass, mica and platinum" *J. Am. Chem. Soc.* 1918; 40: 1361-1403.
11. Redlich, O. and Peterson, D.L., "A useful adsorption isotherm" *J. Phys. Chem.* 1959; 63: 1024-1026.
12. Tempkin, M.J. and Pyzhev, V., "Acta Physiochemical" URSS. 1940; 12: 217-222.
13. Allen, J., Matthews, G. Quan., Pauline, Ronan. Johnson, A., "Comparison of optimized isotherm models for basic dye adsorption by kudzu Stephen". *Bioresource Technology.* 2003; **88:143-152.**
14. Marquardt, D.W., "An algorithm for least squares estimation of non-linear parameters". *J. Soc. Ind. App. Maths.*1963; 11: 431-441
15. D. Bastani, A.A. Safekordi, A. Alihosseini, and V.Taghikhani, Study of oil sorption by expanded perlite at 298.15 K". *Separation and Purification Technology.* 2006;
16. Al-Duri, B. and McKay, G., " Basic dye adsorption on carbon using a solid phase diffusion model" *Chem. Eng. J.* 1988; 38: 23-31
17. Moon, H. and Lee, W.K., " Intraparticle diffusion in liquid phase adsorption of phenols with activated carbon in a finite batch absorber". *J. Colloid. Interface Sci.* 1983; 96: 162-170.
18. Khans, A.R., Al-Bahri, T.A., Al-Haddad, A., "Adsorption of phenol based organic pollutants on activated carbon from multicomponent dilute aqueous solutions". *Water Res.*1997; 31: 2101-2112

Nomenclature

a_L	Langmuir isotherm constant ($\text{dm}^3 \text{mg}^{-1}$)
a_R	Redlich-Peterson isotherm constant ($\text{dm}^3 \text{mg}^{-1}$)
A	Tempkin isotherm constant
b	
b_F	Tempkin isotherm energy constant (J mol^{-1})
b_F	Freundlich isotherm exponent

B	Tempkin isotherm energy constant ($\text{dm}^3 \text{g}^{-1}$)
C_0	Initial liquid-phase concentration (mg dm^{-3})
C_e	Equilibrium liquid-phase concentration (mg m^{-3})
ERRSQ	The sum of the squares of errors
HYBRID	The hybrid fractional error function
K_F	Freundlich isotherm constant ($\text{dm}^3 \text{g}^{-1}$)
K_L	Langmuir constant ($\text{dm}^3 \text{g}^{-1}$)
K_R	Redlich–Peterson isotherm constant ($\text{dm}^3 \text{g}^{-1}$)
MPSD	Marquardt's percent standard deviation
n	Number of isotherm parameters
p	Number of data points
q_e	Equilibrium solid-phase concentration (mg g^{-1})
Q_0	Monolayer capacity of Langmuir equation (mg g^{-1})
$q_{e, \text{calc}}$	Calculated dye equilibrium solid phase concentration (mg g^{-1})
$q_{e, \text{meas}}$	Measured dye equilibrium solid phase concentration (mg g^{-1})
R	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	Temperature (K)
β	Exponent in Redlich–Peterson isotherm

Captions for figures

Figure 1 langmuir isotherm and model data; ▲ Medium Asian, ◆ Iranian Oil light, □ Model data

Figure 2 Frundlich isotherm and model data; ▲ Medium Asian, ◆ Iranian Oil light, □ Model data

Figure 3 Redlich- Peterson isotherm and Model data; ▲ Medium Asian, ◆ Iranian Oil light, □ Model data

Figure 4 Temkain isotherm and experimental data; ▲ Medium Asian, ◆ Iranian Oil light, □ Model data

Table 1. Langmuir isotherm constants a_L and K_L and errors function

Oil Type	a_L	K_L	R^2	Chi-Square
I. O. L	6.584×10^{-2}	0.42311	0.9132	9.2314×10^{-1}
M. As	7.248×10^{-2}	0.4756	0.9356	1.152×10^{-1}
Oil Type	ERAV	ERRSQ	HYBRID	MPSD
I.O.L	2.3645	0.7860075	1.073953	10.36317
M. As	2.5463	0.82314	1.15243	11.4567

Table 2. Freundlich isotherm constants K_f and b_f and errors function

Oil Type	K_F	b_f	R^2	Chi-Square
I. O. L	2.531	0.23278	0.989	5.8513×10^{-2}
M. As	2.7846	0.2506	0.988	6.54×10^{-2}
Oil Type	ERAV	ERRSQ	HYBRID	MPSD
I. O. L	0.928562	1.081×10^{-2}	6.5227×10^{-3}	0.8078
M. As	0.98251	1.15×10^{-2}	8.754×10^{-3}	0.9423

Table 3. Redlich-Peterson isotherm constants K_R , a_R , β , R^2 and errors function

Oil Type	K_R	a_R	β	R^2	Chi-Square
I.O.L	5.190622	1.90345	0.78	0.999	1.025×10^{-2}
M. As.	5.092	2.0452	0.79	0.999	4.32×10^{-2}
Oil Type	ERAV	ERRSQ	HYBRID	MPSD	
I.O. L	0.1927	9.445×10^{-3}	1.132×10^{-3}	0.7254	
M. As	0.2841	7.458×10^{-3}	7.674×10^{-3}	0.9843	

Table 4. Tempkin isotherm constants A, B, R^2 and errors function

Oil Type	A	B	R^2	Chi-Square
I.O.L	12	0.6678	0.98	4.2664×10^{-2}
M.As	14	0.7845	0.974	4.537×10^{-2}
Oil Type	ERAV	ERRSQ	HYBRID	MPSD
I.O.L	0.3105	8.3224×10^{-2}	1.410318×10^{-1}	3.7554
M.As	0.98251	2.5×10^{-2}	9.724×10^{-2}	4.658

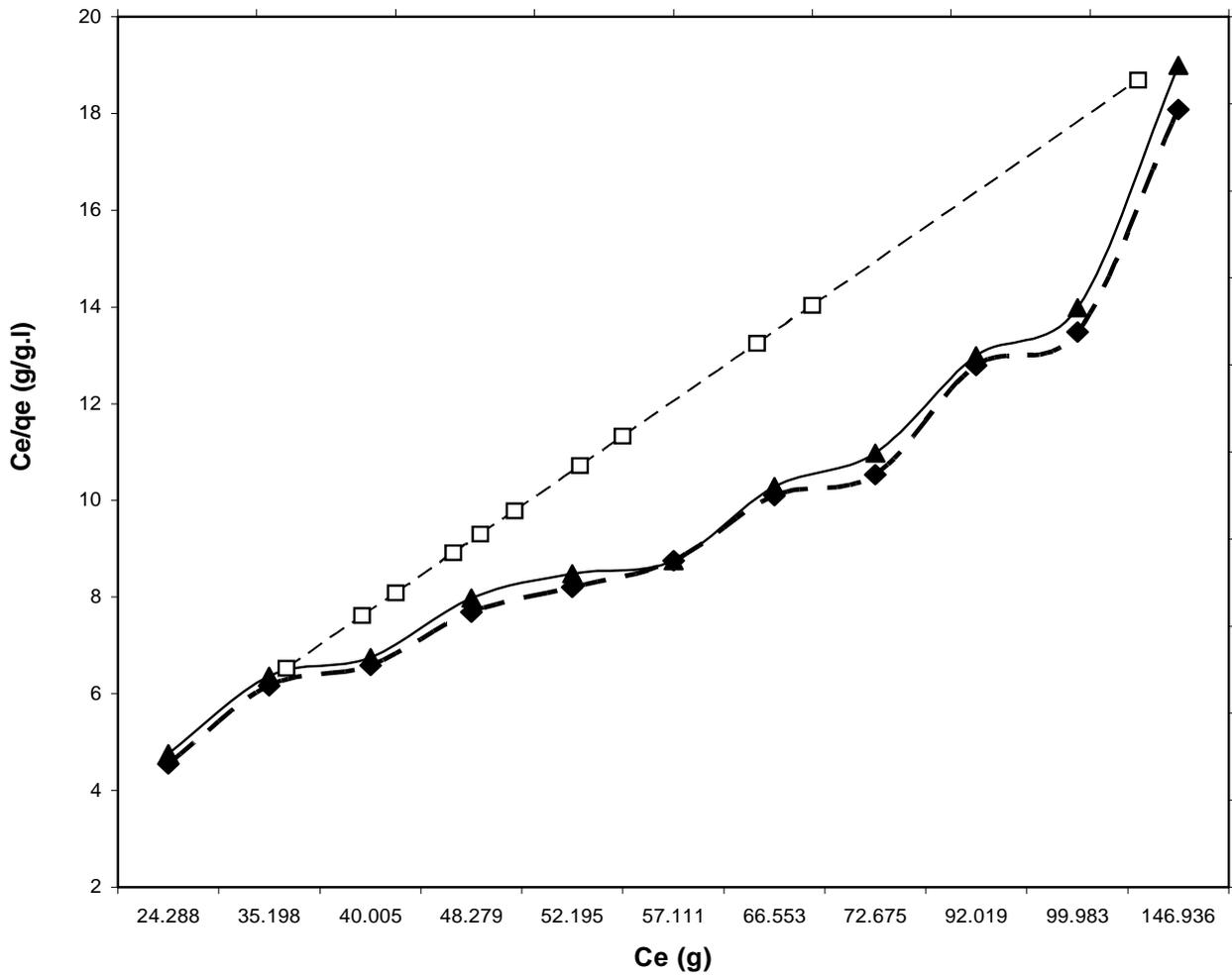


Fig.1

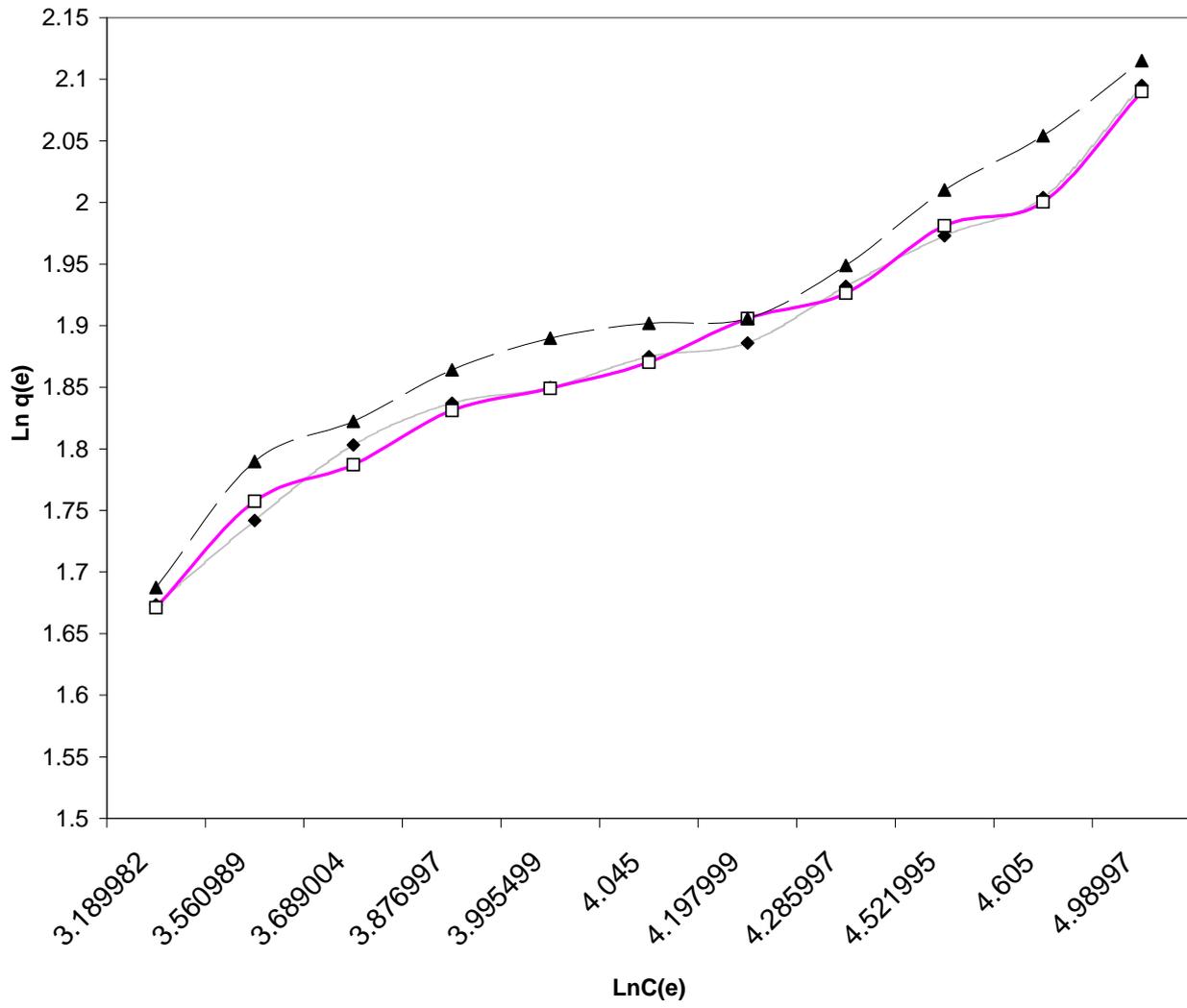
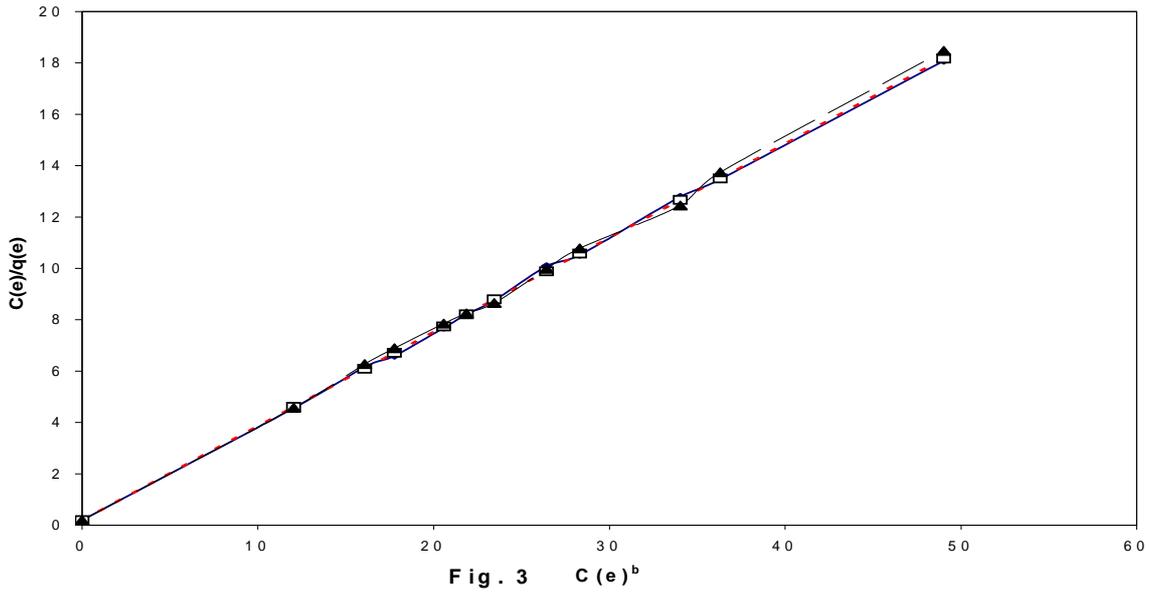


Fig. 2



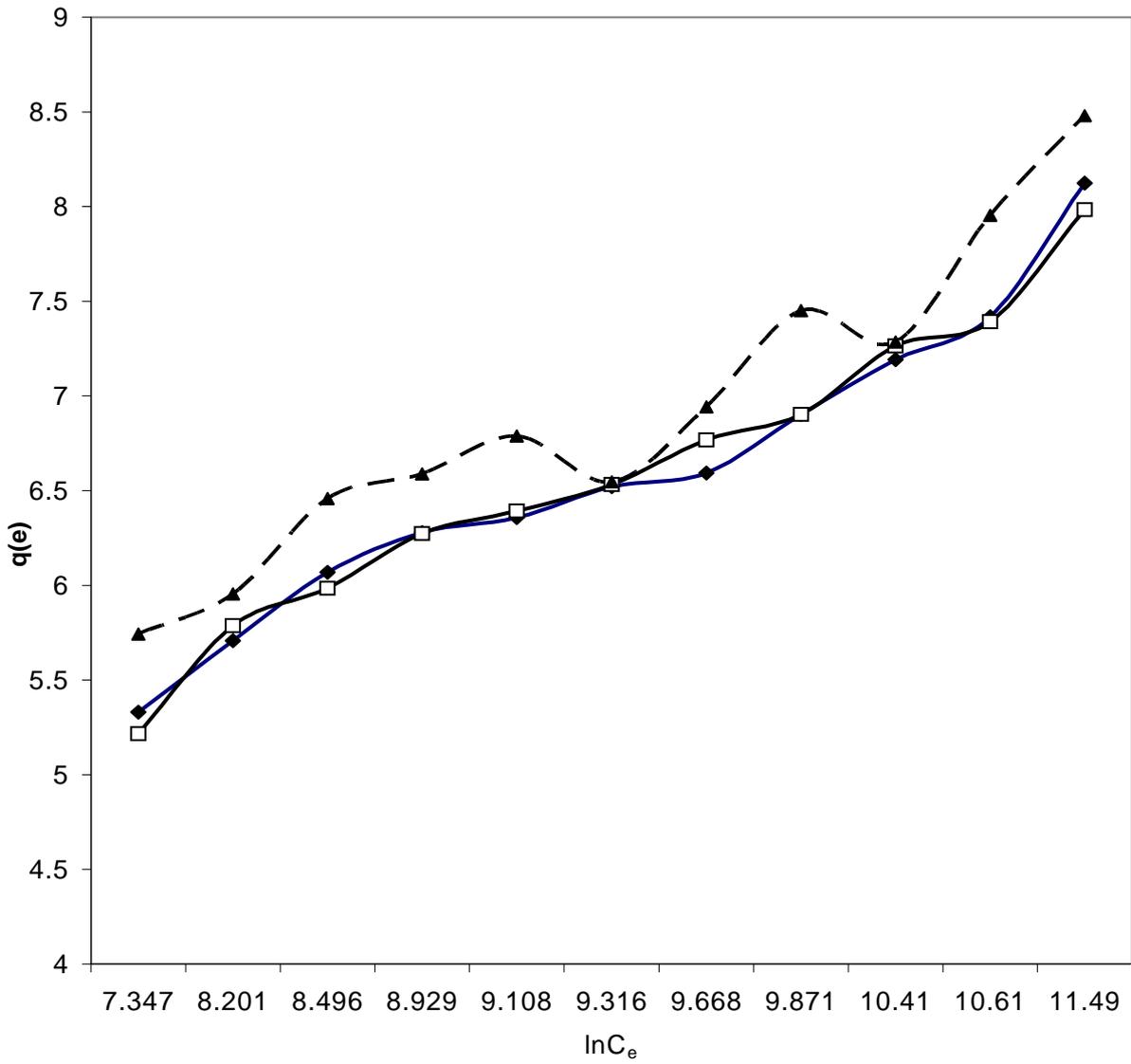


Fig 4.

This document was created with Win2PDF available at <http://www.daneprairie.com>.
The unregistered version of Win2PDF is for evaluation or non-commercial use only.