Freundlich Adsorption Isotherm in the Perspective of Chemical Kinetics (III): Isolation Method Approach

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ABSTRACT. Determination of Freundlich Adsorption Isotherm (FAI) fitting-constant is mostly carried out using different amounts of adsorbent with fixed amount of adsorbates, calculated for 1 g or 1 mgr, and measured at the same contact time. This technique is used together with Langmuir Adsorption Isotherm (LAI). It is considered empirical but, kinetically, it is similar to the Isolation Method (IM). The purpose of this study is to provide a theoretical basis for the use of the IM approach in conjunction with LAI based for FAI fitting-constant determination and provide suggestions for data analysis techniques. The study was carried out theoretically, while the validity test was carried out by applying the findings to the literature data which were supplemented by statistical tests. The results show that the present technique is somewhat dubious. The technique is not suitable for every adsorbent-adsorbate pair (violating the basic assumptions of the LAI kinetics aspect) and the non-linear analysis technique give an order-reaction that is not always consistent with the adsorption condition. A new technique has been introduced. This new technique gives a value of \( b = n \) (Percentage Difference, \( PD \), is less than 5%).

1. Introduction

The Freundlich Adsorption Isotherm (FAI), one of the first isotherms equations introduced to describe the adsorption phenomena, is given in equation:

\[
S = KC^b
\]

(1)

where \( S \) is mass adsorbed per adsorbent mass, \( C \) is concentration in solution, and \( K \) and \( b \) are fitting-constants. \( S \) is an intensive properties. The fitting-constant \( b \) is dimensionless.

EQ. (1) has no theoretical foundation [1, 2]. It is empirical and have nearly no, or limited in its usefulness for its ability to fit data or to interpret the physical significance of the coefficients. The value of \( K \) is obtained from the intercept and \( b \) from the slope of the double-logarithmic plot of log \( S \) versus log \( C \) of equation:

\[
\log S = \log K + b \log C
\]

(2)

The kinetic approach has also been introduced [3]. It is based on equation:

\[
-\frac{dC}{dt} = k_1C^n - k_2S^n
\]

(3)

At equilibrium the derivative is equal to zero. Then, after some steps EQ. (3) becomes:
\[ S = (k_1 / k_2)^{1/n_2} C^{n_2} \quad (4) \]

where \( n_1 \) and \( k_1 \) are the order and fractal rate constant for adsorption and \( n_2 \) and \( k_2 \) for desorption. \( EQ. (4) \) is identical with \( EQ. (1) \) if \( (k_1/k_2)^{1/n_2} = K \) and \( (n_1/n_2) = b \). However, it is unlikely that the rate of adsorption is independent of \( S_0 \).

A more acceptable derivation has been given. It is based on equation:
\[ -\frac{dC}{dt} = k_1 (S_o - S) C^{n_1} - k_2 S \quad (5) \]

where \( S_o \) is the maximum adsorbed. If \( S \ll S_o \) and at equilibrium, after some steps, \( EQ. (5) \) becomes:
\[ S = \left[ \frac{k_1}{k_2} \right] S_o C^{n_1} \quad (6) \]

where \( n_1 \) is the fractal dimension for adsorption. Here, the fractal dimension with respect to adsorption \( (S_o) \) and desorption \( (S) \) are assumed to be first-order for \( EQ. (6) = EQ. (1) \) if \( (k_1/k_2)S_o = K \) and \( n_1 = b \) [4].

\( EQ. (1) \) is usually used together with the Langmuir Adsorption Isotherm (LAI):
\[ S = \frac{K_{ads} C}{k + C} \quad (7) \]

or with its fractal form
\[ S = \frac{K_{ads} C^b}{k + C^b} \quad (8) \]

to find the equation that works better for a data, LAI or FAI. It is important to note that both \( EQ. (7) \) and \( EQ. (8) \) are derived by kinetics approach [5, 6].

\( EQ. (1) \) can also be derived from \( EQ. (8) \). If \( C^b \ll k \), \( EQ. (8) \) becomes
\[ S = \frac{K_{ads} C^b}{k} \quad (9) \]

\( EQ. (9) = EQ. (1) \) if \( K_{ads}/k = K \). From kinetics point of view, the reaction is of the \( b \)th-order with respect to adsorbate \( C \).

Based on \( EQ. (6) \) and \( EQ. (9) \), FAI is LAI at low adsorption and \( n = b \). Despite the claim that the value of \( 0 < b < 1 \) [7, 8], it has been proved that the fitting constant \( b \) represents the same meaning with reaction order \( n \) [9, 10]. So, there is no need to check whether an adsorption process works better for FAI or LAI [11].

The \( k \) value can be determined from the intercept of the plot of:
\[ \log S = \log \left( \frac{K_{ads}}{k} \right) + b \log C \quad (10) \]

The value of \( K_{ads} \) is determined from the condition of \( C^b \gg k \). In this condition,
\[ S = K_{ads} \quad (11) \]

By \( EQ. (11) \), the reaction is of the \( zeroth \)-order with respect to adsorbate concentration [12].
The determination of the FAI fitting-constant is mostly carried out by using different amounts of adsorbent with the same amount of adsorbate, calculated for 1 g or 1 mgr, and measured at the same contact time. This technique is considered empirical but, kinetically, is similar to the isolation method.

There are 2 interesting problems arise. First, as has been discussed, dividing the equilibrium concentration with the amount of adsorbent used is not valid for every condition. It is depend on the reaction order with respect to adsorbent. Theoretically will only valid for first-order reaction. This facts can be related to isolation method.

Second, there is no definite requirement regarding the ratio of the amounts of adsorbates and adsorbents used; in the condition of \( C^b \ll k \), or \( C^b \gg k \), or in both conditions. But, by EQ. (9), FAI is valid only if \( C^b \ll k \). Then, the 3 cases can cause confusion in analytical techniques, linear or non linear.

Based on the above discussion, there are two objectives of this study.
1. To identify the possible error made by the method carried out by using different amount of adsorbents under fixed amount of adsorbates.
2. To clarify the use of data analysis techniques by linear and non linear method.

2. Experimental

2.1. Data

This research is a literature study. The data used are presented in Table 1 [13], Table 2 [14], and Table 3 [15]. Discussion will be focused on the determination of FAI fitting-constant that based on the LAI and or fractal-LAI model. More specifically on the effect of the amount of adsorbent used.

| Table 1. Effect of the amount of Adsorbent on the adsorption of Acetic Acid at 298 °K and Contact Time 90 Minutes |
| G | Amb. | IRA-67 | \( C_o \) | \( C_e \) | \( S_e \) | \( C_e \) | \( v \) | \( v \) |
|---|---|---|---|---|---|---|---|---|
| G | g. L^{-1} | g. L^{-1} | g. mg^{-1} | M | M min^{-1} | M min^{-1}g^{-1} |
| 0.25 | 105.60 | 94.20 | 0.0456 | 1.570 | 2.11x10^{-3} | 8.44x10^{-3} |
| 0.50 | 105.60 | 85.50 | 0.0402 | 1.425 | 3.72x10^{-3} | 7.44x10^{-3} |
| 0.75 | 105.60 | 74.40 | 0.0416 | 1.240 | 5.78x10^{-3} | 7.71x10^{-3} |
| 1.00 | 105.60 | 69.60 | 0.0360 | 1.160 | 6.67x10^{-3} | 6.67x10^{-3} |
| 1.25 | 105.60 | 61.20 | 0.0355 | 1.020 | 8.22x10^{-3} | 6.58x10^{-3} |
| 1.50 | 105.60 | 54.60 | 0.0340 | 0.910 | 9.44x10^{-3} | 6.29x10^{-3} |
| 1.75 | 105.60 | 46.20 | 0.0340 | 0.770 | 1.08x10^{-2} | 6.29x10^{-3} |

PS:  
1. In the original data, the contact time is not given. The time 90 minutes is taken from the data of the effect of contact time of Acetic Acid.  
2. In other to have the same condition with other, only 7 of the 8 data used.  
3. The results show that the LAI fits the experimental data but give negative value for \( K_L \) (= \( K_{ads} \)).

| Table 2. Effect of the amount of Granular Activated Carbon, GAC, on the adsorption of Soluble Organic Nitrogen at 293 °K and Contact Time 2 Hours |
| GAC | \( C_o \) | \( C_e \) | \( S_e \) | \( C_e \) | \( v \) | \( v \) |
| Mg | mg. L^{-1} | mg. L^{-1} | mg. mg^{-1} | M | M hour^{-1} | M hour^{-1}g^{-1} |
|---|---|---|---|---|---|---|
| 0.2 | 0.90 | 0.77 | 0.65 | 1.283x10^{-5} | 1.08x10^{-6} | 5.42x10^{-6} |
| 0.5 | 0.90 | 0.65 | 0.500 | 1.083x10^{-5} | 2.08x10^{-6} | 4.17x10^{-6} |
| 2.0 | 0.90 | 0.32 | 0.290 | 5.33x10^{-6} | 4.83x10^{-6} | 2.42x10^{-6} |
| 5.0 | 0.90 | 0.19 | 0.142 | 3.17x10^{-6} | 5.92x10^{-6} | 1.18x10^{-6} |
| 10.0 | 0.90 | 0.14 | 0.076 | 2.33x10^{-6} | 6.33x10^{-6} | 6.33x10^{-6} |
| 20.0 | 0.90 | 0.09 | 0.041 | 1.50x10^{-6} | 6.75x10^{-6} | 3.38x10^{-6} |
| 50.0 | 0.90 | 0.06 | 0.017 | 1.00x10^{-6} | 7.00x10^{-6} | 1.40x10^{-6} |
PS: The results of calculation show that the \( \text{FAI} \) fits the experimental data but give negative value for \( q_m (= K_{ads}) \) and \( b = 0.32 \).

### Table 3. Effect of the amount of Activated Carbon, AC, on the adsorption of Methylene Blue at 298 \(^\circ\)K and Contact Time 72 Hours

| AC (mg) | \( C_0 \) (mg/L) | \( C_e \) (mg/L) | \( S_e \) (mg/mg) | \( C_v \) (M) | \( v \) (M hour\(^{-1}\)) | \( v \) (M hour\(^{-1}\)) |
|--------|-----------------|-----------------|-----------------|--------------|-----------------|-----------------|
| 1      | 25              | 19.9            | 5.1             | 6.22x10^{-2} | 2.21x10^{-4}   | 2.21x10^{-4}   |
| 5      | 25              | 10.8            | 2.84            | 3.38x10^{-2} | 6.16x10^{-4}   | 1.23x10^{-4}   |
| 10     | 25              | 4.2             | 2.08            | 1.31x10^{-2} | 9.03x10^{-4}   | 9.03x10^{-5}   |
| 12.5   | 25              | 3.5             | 1.72            | 1.09x10^{-2} | 9.33x10^{-4}   | 7.46x10^{-5}   |
| 25     | 25              | 1.0             | 0.96            | 3.13x10^{-3} | 1.04x10^{-3}   | 4.16x10^{-5}   |
| 30     | 25              | 0.70            | 0.81            | 2.19x10^{-3} | 1.06x10^{-3}   | 3.53x10^{-5}   |
| 100    | 25              | 0.20            | 0.248           | 6.25x10^{-4} | 1.08x10^{-3}   | 1.08x10^{-5}   |

PS: The stress of this article is not for determining the better isotherm that fits for the experimental data. But the results show \( \text{LAI} \) fits better and linear and non-linear method give different values for the fitting-constant.

2.2. Framework and execution technique

2.2.1. First case.

Determination of the reaction order for each reagent whose reaction rate depends on the concentration of two (or more reagents) is difficult to do simultaneously. The Isolation Method (IM) is the solution.

For simplest case:

\[
v = k [A_o]^a[B_o]^b\tag{12}
\]

If \([A_o]\) is made much smaller than \([B_o]\): say one hundredth, because \([B]\) is practically unchanged, the rate law becomes

\[
v = k' [A_o]^a\tag{13}
\]

where

\[
k' = k [B_o]^b\tag{14}
\]

The reaction has pseudo order \( a \). The value of \( k' \) is obtained from the intercept of the plot of \( \log [A_o] \) versus \( \log v \) [of \( EQ. (13) \)].

There are 2 ways to obtain \( b \). But, to the extent used in this study, \([B_o]\) is still made higher, say, two fold. Then, the rate law becomes

\[
v = k'' [A_o]^a\tag{15}
\]

where

\[
k'' = k [2B_o]^b\tag{16}
\]

The reaction also has pseudo order \( a \). The value of \( k'' \) is obtained from the intercept of the plot of \( [A_o] \) versus \( \log v \) [of \( EQ. (15) \)]. Then, the value of \( b \) is obtained using \( EQ. (14) \) and \( EQ. (16) \). That is to say, 2 data are enough for \( b \) determination. As for this study, because \([A_o]\) are made all same and \( a \) does not change, then the value of \( b \) is determined from the slope \( \log [B_o] \) versus \( \log v \) of \( EQ. (12) \). However, because basically in \( EQ. (6) \), \( EQ. (7) \), and \( EQ. (8) \), the value of \( b \) is 1 (first-order), this value is then used as the standard for evaluating the \( b \) value obtained. Also, because the reaction-order can only be integers or half-integers [16, 17], the values obtained are then rounded to the closest order. The result of calculation is presented in Table 4.
2.2.2. Second case.
Based on above discussion, there are 2 points to be discussed. 1. The validity of non-linear analysis. 2. As can be seen later, by the New Technique, LAI or fractal-LAI and FAI are valid for Acetic Acid but not for both Soluble Organic Nitrogen and Methylene Blue. The result of calculation is presented in Table 5.

3. Results and discussions
3.1. Results
3.1.1. First case

Table 4. Effect of the Amount of Adsorbent on the Reaction Order, n, with Respect to Adsorbent for Acetic Acid, Soluble Organic Nitrogen, and Methylene Blue by Conventional and Improved Technique

| Adsorbate                  | Theory | Conventional |                  |                  |                  |
|----------------------------|--------|--------------|------------------|------------------|------------------|
|                            |        | All Data     | First 3 Data     | Last 3 Data      |
| Acetic Acid                | 1      | 0.84 ≈ 1     | 0.91 ≈ 1         | 0.84 ≈ 1         |
| Soluble Organic Nitrogen   | 1      | 0.34 ≈ 0.5   | 0.65 ≈ 0.5       | 0.06 ≈ 0         |
| Methylene Blue             | 1      | 0.35 ≈ 0.5   | 0.62 ≈ 0.5       | 0.02 ≈ 0         |

As seen in Table 4, there are 2 terms, Conventional and New Technique. Term Conventional is used for representing the conventional method while New Technique for method that dividing data into 2 part; at the out-set and near-end. This is because, adsorption data that fits the LAI or fractal-LAI, takes place in two different reaction mechanisms. If the adsorbed is still small (S<<S₀), adsorption is of the bth-order with respect to adsorbate concentration (and so fit FAI). But if if all surfaces covered, than the adsorption is of zeroth-order [18]. Of the the 3 adsorbates, only the Acetic Acid that meets the criteria (n = 1), both by Conventional or New Technique.

3.1.2. Second case

Table 5. Results of Statistical Analysis for b and n by Conventional and New Technique for Acetic Acid, Soluble Organic Nitrogen, and Methylene Blue

|                  | Conventional |                  |                  |                  |
|------------------|--------------|------------------|------------------|------------------|
|                  | All Data     | First 3 Data     | Last 3 Data      |
| Acetic Acid      | 0.409 ≈ 0.5  | 0.345 ≈ 0.5      | 0.142 ≈ 0.0      |
| Soluble Organic Nitrogen | 1.373 ≈ 1.5 | -                | -                |
| Methylene Blue   | 0.601 ≈ 0.5  | -                | -                |

As seen in Table 5, there is no result given for both Soluble Organic Nitrogen and Methylene Blue. As for Acetic Acid, the New Method gives the acceptable value $b = n$ (Table 6) for the fitting-constant of FAI (the first three data). The value of b is obtained from the slope and K from the intercept of EQ. (2). To have the same condition in b determination, the value of n is determined from the slope of the plot of log C₀ (column 5) versus log ν (column 7) of the data.

The proof of compatibility of K and the rate constant $k$ value can also be obtained using equation:

$$\Delta t k [MW]^{1-n} \frac{w_{ads}}{v} = K$$  \hspace{1cm} (17)
where $\Delta t$, $k$, $MW$, $n$, $w_{ads}$, and $K$ are the time, rate constant, molecular weight of the adsorbate, reaction-order, (mean) weight of the adsorbent, and $FAI$ fitting constant (19). Results of calculation is presented in Table 6.

| $b$     | $n$     | $K$     | $k$     | $K_{eq}$ (17) |
|---------|---------|---------|---------|--------------|
| 0.345   | 0.339   | 9.19x10^{-3} | 7.00x10^{-3} | 9.43x10^{-3} |

$PD$ % 1.74 2.61

Relatively each pair of $b$ and $n$ and $K$ and $k$ has the same value. These meant that $b$ and $n$ concepts represent the same idea.

3.2. Discussion

There are not enough facts to explain why Acetic Acid meets the criteria and two other not. Probably depend on the structure and nature of each adsorbate and adsorbent; not on the ratio of adsorbent use. The facts that both Soluble Organic Nitrogen and Methylene Blue are not appropriate for the New Technique does not have to mean that the isolation method is not suit for $FAI$ fitting-constant determination. The amount of reactants reacted or products obtained at any time, can always be calculated using the rate constant, $k$, value. Moreover, the facts that the Last 3 Data show that adsorption is independent of the amount of adsorbent and can be used to determine maximum adsorption.

It is of the first interest to discuss the facts presented in Table 5 and Table 6. In Table 5, for Acetic Acid, the First 3 Data gives half-order, which meant that Acetic Acid dissociated before being adsorbed. Because, the Last 3 Data gives zeroth-order (so as in column 4 (Table 1) than these three data give the value of $K_{ads}$ (of $LAI$). These 2 facts at once proofed that non-linear analysis technique is not appropriate for $FAI$ fitting-constant determination in its conjunction with $LAI$. The non-linear analysis give $b$ or $n$ which is always the same with that using data at the out-set and near end of adsorption. (There are 3 possible situation. If both First 3 Data and Last 3 Data give $n \neq 0$ -integers or half-integers- then the data only fit for $FAI$. If First 3 Data gives $n = 1$ and Last 3 Data gives $n \neq 0$, then the data fit for $FAI$ and $LAI$. And, if both First 3 Data and Last 3 Data give $n = 0$, then the data fit only for $LAI$). Facts in Table 6 prove that the concepts of $b$ and $n$ representing the same idea.

4. Conclusion

Kinetically, the method with the use of different amounts of adsorbent under fixed adsorbate conditions is not always appropriate for fractal-$LAI$ based of $FAI$ fitting-constant determination. Non-linear data analysis technique is not suited for fractal-$LAI$ based of $FAI$ fitting-constant determination. A New Technique has been introduced.

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