Derivation and constants determination of the Freundlich and (fractal) Langmuir adsorption isotherms from kinetics

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Abstract. The Freundlich adsorption isotherm is mostly presented as an empirical equation and the (fractal) Langmuir adsorption isotherm is derived from kinetics. However, their constants are determined by thermodynamic approach. As yet, both are used as an independent tool for determining the type of adsorption, just physical or chemical adsorption. This study aims to introduce an alternative way of driving Freundlich adsorption isotherm from kinetics, to elaborate its relation with the (fractal) Langmuir adsorption isotherm, and to determine their constants simultaneously by kinetics approach. An alternative way of determining the constants in both isotherm equations by kinetics approach was introduced. The results were then compared with that obtained by the conventional method. The study is theoretical but the validity of determination technique is based on the statistical tests on data adapted from literature. The Freundlich adsorption isotherm is introduced; the isotherm is the (fractal) Langmuir adsorption isotherm at relatively low concentration. It is irrelevant to use both adsorption isotherm separately. The new method is more reliable and it represent the reaction.

1. Introduction

One of the first isotherm equations introduced to describe the adsorption phenomenon is the Freundlich Adsorption Isotherm (FAI):

\[ S = KC^b \]  

(1)

where \( S \) is the mass adsorbed per adsorbent mass; \( C \) is the concentration in solution; \( K \) and \( b \) are fitting constants [1]. 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 (Eq.):

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

(2)

The other is the Langmuir Adsorption Isotherm (LAI):

\[ S = \frac{K_{\text{ads}}C}{k + C} \]  

(3)

where \( K_{\text{ads}} \), and \( k \) are fitting constants [2,3]. The curve pattern of \( S \) versus \( C \) of (Eq.) (3) is a rectangular hyperbola. Thus, it is difficult to determine the values of \( K_{\text{ads}} \) and \( k \) directly from Eq. (3). By taking the reciprocal of both sides of Eq. (3), however, is transformed into its linear form.
The \( K_{ads} \) value is obtained from the intercept and \( k \) from the slope of the curve \( (1/S) \) versus \( (1/C) \). However, for some reason, Eq. (4) cannot be used to get the exact values of \( K_{ads} \) dan \( k \) [4].

In many textbooks, the FAI is presented as an empirical equation with nearly no, or limited in its usefulness for its ability to fit data or to interpret the physical significance of the coefficient [5]. The kinetics approach has also been introduced [6]. It is based on equation:

\[
- \frac{dC}{dt} = k_1 C^{n_1} - k_2 S^{n_2}
\]

At equilibrium the derivative is equal to zero. Then, after some steps Eq. (5) becomes:

\[
S = (k_1 / k_2)^{1/n_2} C^{n_2}
\]

where \( n_1 \) and \( k_1 \) are the order and fractal rate constant for adsorption and \( n_2 \) and \( k_2 \) for desorption. Eq. (6) is identical with Eq. (1) if \((k_1 / k_2)^{1/n_2} = K \) and \((n_1 / n_2) = b \).

The modified or fractal LAI has also been introduced by the same author. It is based on equation:

\[
- \frac{dC}{dt} = k_1 (S_o - S) C^{n_1} - k_2 S
\]

At equilibrium the derivative is equal to zero. Then, after some steps Eq. (7) becomes:

\[
S = \frac{S_o C^{n_1}}{k_2 / k_1 + C^{n_1}}
\]

where \( S_o \) is the maximum adsorption capacity and \( k_1 \) and \( k_2 \) are the fractal rate constants. Or, if \( S_o = K_{ads} \); \( n_1=b \), and \( k_2/k_1 = k \) becomes

\[
S = \frac{K_{ads} C^b}{k + C^b}
\]

Eq. (9) is the fractal LAI and identical with Eq. (3) if \( b = 1 \). Another form of equation has also been reported earlier [7].

The reciprocal of both sides of Eq. (9) is

\[
1/S = 1/K_{ads} + (k/K_{ads}) C^b
\]

Eq. (10) is identical with Eq. (4) if \( b = 1 \). The value of \( K_{ads} \) is obtained from the intercept of the linear plot of \( 1/S \) versus \( 1/C^b \) and then used to determine \( k \) from the slope of the line.

It is interesting to compare Eq. (10) with the equation obtained from Eq. (9) on the condition of \( C^b \) which is relatively higher and lower than \( k \).

If \( C^b \) is higher than \( k \), then \( C^b + k \approx C^b \), Eq. (9) becomes

\[
S = K_{ads}
\]

The reciprocal of Eq. [11] is
\[ 1/S = 1/K_{\text{ads}} \]  \hspace{1cm} (12)

which is differ with Eq. (10).

Inserting Eq. (12) into Eq. (10) gives

\[ 1/K_{\text{ads}} = 1/K_{\text{ads}} + (k/K_{\text{ads}})1/C^b \]

\[ k = 0 \]  \hspace{1cm} (13)

That is to say, Eq. (10) does not apply if \( C^b \) is relatively higher than \( k \).

If \( C^b \) is lower than \( k \), and so \( C^b + k = k \), Eq. (9) becomes

\[ S = (K_{\text{ads}}/k)C^b \]  \hspace{1cm} (14)

The reciprocal of Eq. (14) is

\[ 1/S = (k/K_{\text{ads}})1/C^b \]  \hspace{1cm} (15)

which is also differ with Eq. (10).

By assumption, \( S_0 = K_{\text{ads}} \) and therefore, if all surfaces occupied (or \( S = S_0 \)), then \( S = K_{\text{ads}} \) and Eq. (15) becomes

\[ k = C^b \]  \hspace{1cm} (16)

That is to say, Eq. (10) also does not apply if \( C^b \) is relatively lower than \( k \). Thus, it can be concluded that, theoretically, Eq. (10) is ambiguous and therefore it cannot be used to determine both \( K_{\text{ads}} \) and \( k \).

There are some problems arises. First, Eq. (6) does not always apply to every reaction. The fitting constant \( b \) has a value of \( 0 < b < 1 \) [8]. But, the reaction orders are usually integers (1, 2, ...) or half-integers (1/2, 3/2, ...), positive or negative [9]. If, \( n_i \) is higher than \( n_j \), then \( b > 1 \). Furthermore, unlike Eq. (7), in Eq. (5), the rate of adsorption is assumed to be independent on the vacant sites, \( S_i (= S_0 - S) \). This goes against theory. Normally, the amount of vacant sites and the types of adsorbent always affect the rate. Thus, the rate of adsorption in Eq. (5), must depend on \( S_i \). Moreover, the order with respect to \( S \) is \( n_j \) but in Eq. (7) is the first-order.

Second, usually the \( FAI \) and \( LAI \) equations are treated separately. For example in determining the type of bond formed in the adsorption process; chemical or just physical bond [10]. However, the \( FAI \) can be derived from \( LAI \) [11]. Allegedly, it is suspected that this statement can be confirmed by using Eq. (9) and Eq. (1). If so, then it is possible to determine the constants of both \( FAI \) and \( LAI \) simultaneously.

Third, as yet, despite being derived from kinetics, the constants in both isotherms are still determined by the thermodynamic approach. The data used are always obtained from equilibrium condition at the same contact time. In practice, by using a certain concentration, the first step is to find the time needed to achieve the equilibrium condition. Then by using the time obtained to find the \( S \) change from some other concentrations. For some reasons, this treatment is not recommended. It is possible that the data are just taken from a certain condition and only valid to Eq. (11) \( i.e. C^b \) is higher than \( k \) or Eq. (14) \( i.e. C^b \) is lower than \( k \). This is not representing the sample as a whole. Basically, the \( S \) concept is resemble to the rate concept; the changes of the amount of reactant or product at a given time interval. To be more specific, it is similar to the differential method in kinetics. The order obtained by differential method is fixed but the value of the constant must be checked with that obtained by integral method [12]. In addition, the only criterion used to determine the validity of the calculation result is based on the
regression coefficient. The result is always claimed to be valid if the regression coefficient is close to ±1.000. It is never questioned whether the data used have met the adsorption isotherm conditions for FAI and/or LAI or not.

Based on the above discussion, the objectives of this study are to derive FAI by kinetics approach, to elaborate the relation of FAI and LAI, and to determine the FAI and LAI constants simultaneously by kinetics approach.

2. Experimental

2.1. Theory

This research is a literature study. The first goal is to drive Eq. (1) from Eq. (7). The second goal is to drive Eq. (1) from Eq. (9). The third goal is to find an easier and reliable technique for the simultaneous determination of b, K, Kads, and k by kinetics approach and will be achieved by the following steps.

i. By Eq. (14), the order (b) is obtained from the slope of the curve of S versus C for b = 1 and 0.5. This because, by kinetics, to get b < 1, the possible orders are 1 or 0.5. The curve should cross the y-axis at y = 0 and x-axis at x = 0 with regression coefficient closer to ±1.000 and intercept closer to y = 0.00. The k value is determined using the slope and Kads obtained by Eq. (2).

The more exact b value (at the conditions of C higher and lower than k) will be obtained by using integral equations:

\[ [A_o] - [A] = akt \quad \text{for } n = 0 \]  
\[ [A_o]^{0.5} - [A]^{0.5} = \frac{1}{2} akt \quad \text{for } n = 0.5 \]  
\[ \ln[A]/[A_o] = -akt \quad \text{for } n = 1 \]

The equation is selected with regression coefficient closer to ±1.000.

ii. The value of Kads is determined simply, by making the curve of S versus C at the conditions needed for Eq. (10) is valid to be used. This is possible because by Eq. (10) the reaction is zeroth-order with respect to C. The curve should cross the x-axis at x = 0. The intercept is the value of Kads. The curve chosen is that with slope closer to x = 0.00 and regression coefficient closer to ±1.000.

2.2. Model

This study uses data, not from adsorption experiment, but taken from the bromination of acetone: 

\[(CH_3)_2CO + Br_2 \rightarrow CH_2COCH_2Br + Br^- + H^+ \]

Br₂ is assumed to be the adsorbate and acetone, A, (which is in excess) is the adsorbent, H' is the catalyst (which is also in excess) to activate acetone.

The mechanism of the reaction has been given [13] and from that, the rate law of

\[ -\frac{d[P]}{dt} = \frac{(k_2/k_1)[A][H^+][Br_2]}{(k_2/k_1)[H'^+] + [Br_2]} \]

If in the beginning, \([Br_2]_0\), is higher than \((k_2/k_1)[H']\) (actually higher than \([H']\) released from acetone), at the early-stage, the reaction is zeroth-order with respect to \([Br_2]\) but at the near-end is first-order. During the reaction process, \([Br_2]\) is decreased while \([H']\) is almost constant (in this reaction \(H' \) acts as a catalyst and is added excessively). At this condition, this reaction is resemble to adsorption reaction. But, if in the beginning, \([Br_2]_0\) is lower than \((k_2/k_1)[H']\), for the same reason, the reaction is always first-order [14; 15].
As seen in Table 1, the data are not presented in concentration unit but in absorbance of Br$_2$ in the solution, measured at $\lambda=400$ nm (absorbance index 160 M$^{-1}$) and room temperature. The data were obtained from the experiment where, originally, [Br$_2$]$_0$ is higher than [H$^+$] released from acetone.

| No. | $t$/s | A   | $t$/s | A   |
|-----|------|-----|------|-----|
| 1   | 10   | 0.483 | 590   | 0.073 |
| 2   | 20   | 0.473 | 600   | 0.066 |
| 3   | 30   | 0.463 | 610   | 0.059 |
| 4   | 40   | 0.454 | 620   | 0.053 |
| 5   | 50   | 0.444 | 630   | 0.048 |
| 6   | 60   | 0.434 | 640   | 0.043 |

In order to make it more similar to the experimental technique on adsorption, each observation which was taken at the same time interval and the observation resulting at the end of one time interval being considered as the initial value for a new time interval. Each direct observation is taken as $C_o$ and the following as $C$. The difference between each pair is taken as $S$ (thus the amount of $S$ is always taken at the same time–interval). The setting of the data is presented in Table 2.

The value of $b$ is determined by integral method using Eq. (17), Eq. (18), and Eq. (19). It was based on the value of regression coefficient (closest to ± 0.00000) and intercept (closer to 0.00). This step is of special important. This is because the reaction proceeds in different order at the early-stage and near-end.

| No. | $t$/s | Early-stage | Near-end |
|-----|------|-------------|----------|
|     |      | $C_o$ | $C$ | $C_o - C = S$ | $C_o$ | $C$ | $C_o - C = S$ |
| 1   | 10   | 0.483 | 0.473 | 0.010 | 590 | 0.073 | 0.066 | 0.007 |
| 2   | 20   | 0.473 | 0.463 | 0.010 | 600 | 0.066 | 0.059 | 0.007 |
| 3   | 30   | 0.463 | 0.454 | 0.009 | 610 | 0.059 | 0.053 | 0.006 |
| 4   | 40   | 0.454 | 0.444 | 0.010 | 620 | 0.053 | 0.048 | 0.005 |
| 5   | 50   | 0.444 | 0.434 | 0.010 | 630 | 0.048 | 0.043 | 0.005 |
| 6   | 60   | 0.434 |       |       | 640 | 0.043 |       |       |

3. Result and Discussion

3.1. Derivation of the FAI Derivation of the Freundlich isotherm is based on the equation:

$$-\frac{dC}{dt} = k_1(S_o - S)C^{n_1} - k_2S$$

In Eq. (5), the order with respect to $S_s (= S_o - S)$ and $S$ are assumed to be first-order because there is no change in the structure of the adsorbent and the adsorption is assumed to be monolayer. It is just a process of bending and releasing of an adsorbate. It is differing with $C$. Here, the order is $n_1$ (which is
can be an integer or non-integer). The mechanism of the bending process of C may be differing. A change in the structure of an adsorbate could happen. As an example, for a given adsorbent, an acid HA will ionize and being adsorbed as its ion. By ionization, \( HA \leftrightarrow H^+ + A^- \), then \( A^- = K_a^{0.5} C^{0.5} \).

If, \( S < S_o \), Eq. (5) becomes

\[
-dC/dt = k_1 S_o C^{n_1} - k_2 S
\]

At equilibrium the derivative is equal to zero. The equation can then be solved for \( S \):

\[
S = (k_1 / k_2) S_o C^{n_1}
\]  

(22)

or, if \( k_1/k_2= k \) and \( S_o = K_{ads} \), then Eq. (22) becomes

\[
S = (K_{ads}/k) C^{n_1}
\]

(23)

Eq. (23) is identical to the standard Freundlich isotherm, Eq. (1), if \( K_{ads}/k = K \) and \( n_1 = b \).

3.2. Relation of FAI and LAI

At high concentration or \( C^b \) is relatively higher than \( k \), Eq. (9) becomes:

\[
S = K_{ads}
\]

(11)

If \( S \) approaches the limiting value or \( S = S_o \), all surfaces are covered and \( S_o = K_{ads} \). From kinetics point of view, the reaction is of the zeroth-order with respect to \( C \).

At low concentration or \( C^b \) is relatively lower than \( k \), Eq. (9) becomes

\[
S = (K_{ads}/k) C^b
\]

(14)

Eq. (14) is identical with Eq. (1) if \( K_{ads}/k = K \). From kinetics point of view, the reaction is of the \( b \)th-order with respect to \( C \). This means, the FAI can be derived from the fractal Langmuir equation; the same as discussed above. The FAI is the LAI at low concentration \( C \).

3.3. Simultaneous determination of LAI and FAI from kinetics

Based on above discussion, it is important to determine the order of the reaction at both conditions; at the early-stage (to determine \( K_{ads} \)) and at the near-end (to obtain \( K_{ads}/k \), and then used to determine \( k \)). This treatment is then called the New Method (NM). For easier calculation, the \( A_n \) for the early-stage is 0.483 and for the near-end is assumed to be 0.073 for \( n = 1 \) and for the early-stage is 0.4830.5 and for the near-end is assumed to be 0.0730.5 for \( n = 0.5 \). The results of the calculation by integral method for \( n = b = 0, 0.5, \) and 1 are presented in Table 3.

### Table 3. Order, \( n = b \), of the Reaction at the Early-stage and Near-end

| Position | Early-stage | Near-end |
|----------|-------------|----------|
| \( n = b \) | \( A \) | \( B \) | \( r \) | \( A \) | \( B \) | \( R \) |
| 0        | 0.00030     | 0.00097  | 0.99984 * | 0.00210 | 0.00057 | 0.99709 |
| 0.5      | -0.00005    | 0.00072  | 0.99976   | -0.00202 | 0.00123 | 0.99897 |
| 1        | 0.00094     | -0.00214 | 0.99965   | 0.00249  | -0.01063 | -0.99981 * |
Based on Table 3, the new method confirms that at the early-stage, the process is zeroth-order \( (r = 0.99984) \) and first-order at the near-end \( (r = 0.99984) \). Thus, by the NM, the value of \( K_{ads} \) is determined from the intercept of the curve of \( S \) versus \( C \) of the data at the early-stage (Eq. 11) and \( k \) from the slope of the curve of \( S \) versus \( C \) of the data at the near-end (Eq. 14). The results are then compared with the values of \( K_{ads} \) and \( k \) obtained by conventional method using Eq. (10) and \( K_{ads} / k \) (obtained from Eq. (14) with \( K \) obtained from Eq. (2)). The results of the determination of \( F/AI \) by conventional (Eq. 2) are presented in Table 4.

**Table 4.** The Results of Statistical Analysis for the Determination of \( F/AI \) Constants

| Data Source | \( A \)  | \( B \)  | \( r \)  |
|------------|--------|--------|--------|
| Early-stage  | -2.01973 | -0.03079 | -0.02212 |
| Near-end    | -1.02415 | 0.94386 | 0.94269 |

The slope \( B \) in Table 4, is used to determine \( b \) (of Eq. (2)). In this case its value is positive. In Table 4, the slope \( B \) at the early-stage is negative. This means that the Freundlich constants \( b \) of the reaction, cannot be determined from the data at the early-stage. Then, the Freundlich constants of the reaction, can only be determined from the data at the near-end.

The slope \( B \) in Table 5, is used to determine \( k /K_{ads} \). Both intercepts have positive value. But, the slope \( B \) at the early-stage is negative. The slope cannot be used to determine \( k /K_{ads} \) of Eq. (4) or Eq. (10) for \( = 1 \). This means that the Langmuir constants of the reaction, can only be determined from the data at the near-end.

**Table 5.** The Results of Statistical Analysis for the Determination of \( L/AI \) Constants

| Data Source | \( A \)  | \( B \)  | \( R \)  |
|------------|--------|--------|--------|
| Early-stage  | 106.5711 | -1.9708 | -0.0297 |
| Near-end    | 9.39179  | 8.47298 | 0.94110 |

The slope \( B \) at the early-stage in Table 6. is close to to zero: the curve is parallel to x-axis and so, the intercept can be used to determine \( K_{ads} \) (of Eq. (11)). The intercept \( A \) at the near-end is close to zero. Then, its slope can be used to determine \( K_{ads} / k \) (of Eq. (14)).

**Table 6.** The Results of Statistical Analysis for the Determination of \( K_{ads} \) and \( k \) by the NM

| Data Source | \( A \)  | \( B \)  | \( R \)  |
|------------|--------|--------|--------|
| Early-stage  | 0.009999 | -0.00043 | -0.01458 |
| Near-end    | 0.00040  | 0.10404 | 0.94039 |

The slope \( B \) at the early-stage in Table 6. is close to to zero: the curve is parallel to x-axis and so, the intercept can be used to determine \( K_{ads} \) (of Eq. (11)). The intercept \( A \) at the near-end is close to zero. Then, its slope can be used to determine \( K_{ads} / k \) (of Eq. (14)).

**Table 7.** The values of \( K_{ads} \) and \( k \) by the Conventional and the NM

| Method   | \( B \) | \( K \)   | \( r \)  | \( K_{ads} \) | \( k \)   | \( r \)  | \( K_{ads} \) | \( K \)  |
|----------|--------|----------|--------|-------------|--------|--------|-------------|--------|
| Early-stage | -     | -        | -      | -           | -      | 0.009999 | -           | -      |
| Near-end | 0.94386 | 0.09459  | 0.94269 | 0.10648     | 0.90217 | 0.94110 | 0.009999 | 0.09602 |
There are five interesting facts reveal in Table 7. that need to be discussed in their relation with the aims of this study.

1. The $FAI$ and $LAI$ constants could not be determined using the conventional method from the data at the early-stage (in the condition of $C > k$). This is consistent with Eq. (11). This means, the constants of $FAI$ and $LAI$ counted by conventional method do not represent the reaction as a whole.

2. By the $NM$, $K_{ads}$ is determined from the data at the early-stage and $k$ from the data at the near-end. These mean, the values of $K_{ads}$ and $k$ determined by the $NM$ represent the reaction as a whole.

3. The value of $b \approx 1$, which is the same as that by integral method, indicates that the $FAI$ is the fractal $LAI$ at low concentration $C$. And, that, relatively, the $K$ value (of $FAI = 0.09459 \approx K_{ads}/k$ (of $LAI = 0.00999 / 0.09602 = 0.10404$). This again confirms the fact that the $FAI$ is a part of fractal $LAI$. (This is because, $FAI$ is determine by differential while $NM$ by integral method)

4. The fact that, at low concentration $C$, $FAI$ has regression coefficient ($r = 0.94269$) higher than $LAI$ ($r = 0.94110$) not just mean, $FAI$ works better than $LAI$ but, simultaneously, confirms that $FAI$ is the fractal $LAI$ at that condition. So, it is irrelevant to distinguish both isotherms.

5. At first sight, the value of $K_{ads}$ and $k$ obtained from the reciprocal of Langmuir equation, Eq. (4), are the real values. Both are higher (than that obtained by $NM$.) However, the data used for the calculation is the data at the near-end (fact 1.) At this condition, $C$ is relatively lower than $k$ and the reaction is first-order; the curve of $S$ versus $C$ cross $x$-axis at $x = 0$ and $y$-axis at $y = 0$. There is no maximum value. $K_{ads}$ can not be determined. Thus, the $NM$ is best used to determine $K_{ads}$ and $k$.

The values given are exact and the process is simple; directly using observation data.

It is interesting to note that the $K_{ads}$ and $k$ values derived from the reciprocal of $LAI$ (Eq. (4)) is approximately ten times higher than that from $NM$. Is it because, unlike $NM$, in Eq. (4), the time factor (in this case 10 seconds) is not included in the calculation? It is unlikely; the value of $K$ (of $FAI = 0.09459$) obtained from Eq. (2) is relatively the same with $K_{ads}/k$ (of $LAI = 0.00999 / 0.09602 = 0.10404$) obtained by using $NM$.

4. Conclusion
In summary, the $FAI$ equation has been derived from kinetics. The equation is the fractal $LAI$ at low concentration $C$. By $NM$, $K_{ads}$ and $k$ of the fractal $LAI$ should be determined separately: $K_{ads}$ from the intercept of the linear plot of Eq. (17): (relatively high $C$) and $k$ from the calculated-value of $K_{ads}$ and the slope of the linear plot of Eq. (19): (relatively low $C$.)

References
[1] Freundlich HMF 1906 Z. Phys. Chem 57 385–470
[2] Langmuir I 1916 Part I The Research Laboratory of The General Electric Company 2221
[3] Langmuir I 1918 Part II The Research Laboratory of The General Electric Company 1848
[4] Patha, Herald E, Hidayat Y, Firdaus M 2016 IOP Conf. Ser. : Mat. Sci Eng. 107 (1)
[5] Spark D L 2003 Environmental Soil Chemistry 2nd (San Diego : Academic Press) pp. 151
[6] Skopp J 2009 J. Chem. Ed. 86 1341-1342
[7] Sposito G 1980 Soil Sci. Soc. Am. J. 44 652-54
[8] Gregory T, Karns C L, Shimizu K D 2005 Anal. Chim. Acta. 528 107-113
[9] Levine I N 2003 Physical Chemistry 6th Edition (New York : McGraw-Hill Companies, Inc) pp. 517
[10] Castellan G W 1983 Physical Chemistry 3rd Edition (Massachusetts : Addison-Wesly Publishing Company, Inc) pp. 428
[11] Sawyer C N, McCarty P L, Parking G N 2003 Chemistry for Environmental Engineering and Science 5th Edition (New York : McGraw-Hill Companies, Inc) pp.100-105
[12] Laidler K J 1987 Chemical Kinetics 3rd Edition (New York : Harper Collins Publisher, Inc) pp. 28
[13] Daniels F, Mathews J H, Williams J W 1970 Experimental Physical Chemistry, 7th Edition (Tokyo: Kogakusha Company, Ltd) pp. 152-155

[14] Patiha 2013 Kajian Kritis terhadap Persamaan-persamaan dan Teknik untuk Penentuan Tetapan Michaelis-Menten Penelitian Fundamental FMIPA UNS (Surakarta)

[15] Patiha, Heraldy E, Hidayat Y, Firdaus M. 2016 IOP Conf. Ser.: Mat. Sci. Eng. 107 (1)