Acta Chimica
&
Pharmaceutica Indica

Acta Chim. Pharm. Indica: 3(3), 2013, 212-218
ISSN 2277-288X

THE SOLUTION OF REVERSIBLE FIRST ORDER REACTION EQUATION REVISITED

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(*Received : 25.10.2011; Accepted : 04.11.2011*)

ABSTRACT

Based on reversible first order reaction model for the description of the variation of the composition of an aqueous metal ion in both the liquid and solid phases, in the presence of an adsorbent, non-linear and linear expressions have been derived for the concentration of an aqueous metal ion. The present expressions are formulated to accommodate the equilibrium (Nnooa) constant to permit its determination from $\frac{[A]}{[A]_o}$ versus time and $\frac{[B]}{[A]_o}$ versus time plots at t = ∞.

Key words: Reversible first-order reaction, Kinetics, Adsorption, Aqueous metal ion, Biosorption.

INTRODUCTION

Inclusion of metals in the environment from various human activities, have been reported to be well above ambient level especially in aquatic environments[1]. Due to the dangers posed by pollution of these aquatic environments by metals, environmental scientists, agencies and non-governmental organizations (NGOs) ensure that education is given on disposal methods and laws enforced so that defaulters are corrected appropriately. It has become necessary therefore to ensure that effluents are treated to remove or reduce pollutants to safe levels, before discharging into the environment.

Treatments of effluents to safe levels before discharging into the environment, have aroused scientific studies to ensure maximum renewal efficiency. Amongst the many treatments available, adsorption is the most promising technique and a feasible alternative[2]. Also, various adsorption kinetic models for studying batch reactions that involve the removal of metals from aquatic environments exist. One of such kinetic models is the reversible first order reaction model[3].

Recent expressions of the solution of reversible first order reaction equation have been obtained[4,5]. Although these expressions can only allow the determination of rate constants (k_1 and k_2). In addition, the existing solution expressions cannot allow the determinations of the rate constants (k_1 and k_2) and equilibrium constant (K) without substitutions into other equation steps that precede the solutions.

A resolution of these problems can be achieved, for the solution of a reversible first order reaction,

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when for example, the plots of the linear forms of the solution are done and from the slope, the rate constants (k_1 and k_2) are obtained. The equilibrium constant can however be obtained when either $\frac{[A]}{[A]_o}$ versus time and $\frac{[B]}{[A]_o}$ versus time plots are made.

This work therefore, sufficiently and exhaustibly presents a clear and complete solution of a reversible first order reaction equation. Highlights on the linear forms that can likely be obtained from the solution will be made also.

Theoretical model for the reversible first order reaction

A simple reversible first-order reaction model can be expressed as[3]:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad \ldots(1)$$

if $[A]_o = [A] + [B]$ are initial boundary conditions.

The rate equation for the reaction can be written as[5]:

$$\frac{d[B]}{dt} = \frac{-d[A]}{dt} = k_1\,[A] - k_2\,[B]$$

$$= k_1\,[A] - k_2\,(\,[A]_0 - k_2\,[A]\,) \qquad \ldots(2)$$

where $[A]_0$ is the initial concentration of metal ion in solution, [B] is the concentration of metal ion on the sorbent and [A] is the concentration of metal ion in the solution at any time. At equilibrium conditions, rate of forward reaction equals rate of backward reaction, hence, $k_1[A] = k_2[B]$. Also, [A] and [B] become $[A]_{eq}$, and $[B]_{eq}$, respectively.

$$\therefore\ \frac{k_1}{k_2} = \frac{[B]_{eq}}{[A]_{eq}} = \text{K = Equilibrium constant} \qquad \ldots(3)$$

From $[A]_o = [A] + [B]$ (initial boundary conditions), $[A]_0$ becomes equal to $[A]_{eq} + [B]_{eq}$ at equilibrium.

$$\therefore\ [B]_{eq} = [A]_o - [A]_{eq} \qquad \ldots(4)$$

Thus, $K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_2} = \frac{[A]_0 - [A]_{eq}}{[A]_{eq}}$, which can be rearranged to make:

$$[A]_{eq} = \frac{k_2[A]_0}{k_1 + k_2} = \frac{[A]_0}{K+1} \qquad \ldots(5)$$

$$\therefore\ \text{Rate} = \frac{-d[A]}{dt} = (k_1 + k_2)\,[A] - k_2\,[A]_0$$

$$= (k_1 + k_2)\,([A] - [A]_{eq.}) \qquad \ldots(6)$$

Equation (6) gives on rearrangement

$\frac{d[A]}{[A]-[A]_{eq}} = -\left(k_1 + k_2\right)dt$ to give the existing solution upon solving the differential equation [4,5]:

$$[A] – [A]_{eq} = ([A]_0 – [A]_{eq})e^{-(k_1 + k_2)t} \qquad …(7)$$

The linear form of equation (7) can be expressed as -

$$\text{In}\left(\frac{[A]-[A]_{eq}}{[A]_0-[A]_{eq}}\right) = -\left(k_1+k_2\right)\, t \qquad …(8)$$

Whatever is the expression of the solution of reversible first order reaction equation, to the best of our knowledge, we have not known of any of the type, we are to derive.

The solution of reversible first order reaction and experimental expressions for the reaction parameters

The sorption of metal ion from liquid phase to solid may be considered as reversible reaction with an equilibrium state between two phases[3]. Exploring the variation of the metal ion composition, in both the liquid and solid phases, can be possible invoking equation (1).

The total volume of the system should be kept constant, initial metal ion concentration of A is $[A]_0$, [B] should not be present initially, and both forward and reverse reactions must be first order[4]. The equation that represents a reversible first order reaction equation-equation (1), can therefore be solved to give

$$[A] = [A]_{eq} + ([A]_0 – [A]_{eq})e^{-(k_1+k_2)t} \qquad …(9)$$

which has a linear form as equation (8). Also, another solution to equation (1)[4] is:

$$[A] = [A]_o \left(\frac{k_2+k_1e^{-(k_1+k_2)t}}{k_1+k_2}\right) \qquad …(10)$$

It is clear that the existing solutions of the reversible first order reaction [equations (9) and (10)], do not contain the equilibrium constant (K). We therefore attempt to include this in expressions that represent the solution of a reversible first order reaction.

To achieve this, a substitution is made in equation (8) from equation (5) to give the following expressions that we wish to refer to as Nnooa equation.

$$\text{In}\left(\frac{[A]-[A]_{eq}}{[A]_{eq}K}\right) = -\left(k_1+k_2\right)\, t \qquad …(11)$$

Equation (11) can be rearranged to give other Nnooa equations, in non-linear form -

$$[A] = [A]_{eq}\ (1 + Ke^{-(k1+k2t})) \qquad …(12)$$

which is equivalent to –

$$[A] = \frac{[A]_o}{K+1}\left(1+Ke^{-(k_1+k_2)t}\right) \qquad …(13)$$

Rearranging equation (11) gives –

$$\text{In}\left(\frac{[A]-[A]_{eq}}{[A]_{eq}}\right) = In\,K - \left(k_1+k_2\right)\, t \qquad …(14)$$

and In $\left(\frac{[A]_{eq}}{[A]-[A]_{eq}}\right) = (k_1 + k_2)\ t - In\,K$ …(15)

Equations (11), (12), (13), (14) and (15) are the required Nnooa equations (derived solutions) from which Nnooa constant (K) particularly and the rate constants-k_1 and k_2, can be obtained. However, equations (14) and (15) are the linear forms of our derived solutions to a reversible first order reaction.

From equation (11), like a straight line equation, plot of in$\left(\frac{[A]-[A]_{eq}}{[A]_{eq}}\right)$ versus time, should give a negative slope from which k_1 + k_2 is obtained. The expressions for determinations of k_1 and k_2 from In$\left(\frac{[A]-[A]_{eq}}{[A]_{eq}}\right)$ versus time plot are –

k_2 = $\frac{-Slope}{1+e^{\text{int}\,ercept}}$ …(16)

Hence, $k_1 = -(k_2 + \text{slope})$ …(17)

Alternatively, plotting In $\left(\frac{[A]_{eq}}{[A]-[A]_{eq}}\right)$ versus time, from equation (15), should give a positive slope equal to $k_1 + k_2$.

Plot of ln $\left(\frac{[A]_{eq}}{[A]-[A]_{eq}}\right)$versus time gives slope and intercept values that can be used in the following expressions for the determinations of k_1 and k_2.

k_1 = $\frac{slope}{1+e^{\text{int}\,ercept}}$ …(18)

and k_2 can be evaluated from –

k_2 = slope – k_1 …(19)

From the foregoing, the determinations of the forward and reverse rate constants- k_1 and k_2, have been deduced. Their determinations by substitution into equation (5) are therefore not necessary.

Henceforth, we highlight how Nnooa constant (K) can be obtained as contained in our solution expressions for reversible first order reaction.

From equation (13), we can obtain –

$$\frac{[A]}{[A]_o} = \frac{1}{K+1}\left(1 + Ke^{-(k_1+k_2)t}\right) \quad \text{…(20)}$$

At time zero (t = 0), equation (20) collapses to –

$$\frac{[A]}{[A]_o} = \frac{1}{K+1}\left(1 + Ke^{0}\right) = 1 \quad \text{…(21)}$$

But at infinitely large time (t = ∞), equation (20) becomes –

$$\frac{[A]}{[A]_o} = \frac{1}{K+1}\left(1+Ke^{-\infty}\right) = \frac{1}{K+1} \qquad \ldots(22)$$

Therefore, a graphical representation of equations (21) and (22) is thus:

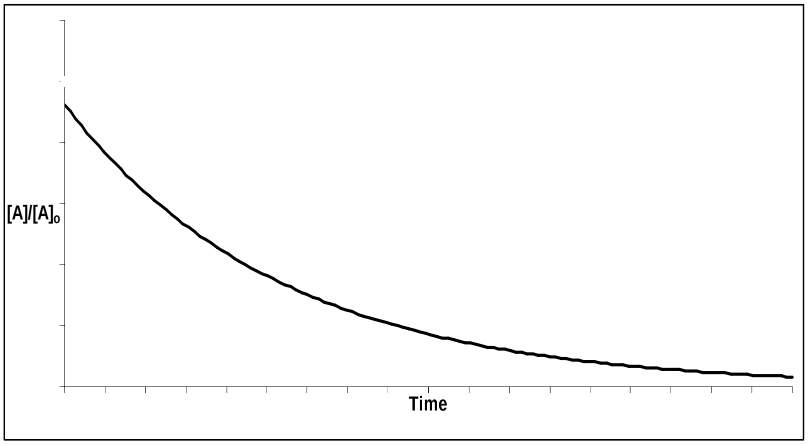

Fig. 1: Variation of $\left(\frac{[A]}{[A]_o}\right)$ with time

As revealed by equation (22), at large enough time, $\left(\frac{[A]}{[A]_o}\right)$ versus time plot becomes $\frac{1}{K+1}$. This can enable the determination of K!. Value of $\left(\frac{[A]}{[A]_o}\right)$ at t = 0 had been predicted[4,5] but its value at t = ∞, to the best of our knowledge, has not been reported until now.

It can be recalled that $[A]_o = [A] + [B]$ (initial boundary conditions).

Therefore, $[B] = [A]_o - [A]$ …(23)

and $[B] = [A] - \frac{[A]_o}{K+1}\left(1+Ke^{-(k_1+k_2)t}\right)$ …(24)

From equation (24), expression for [B] can be obtained as –

$$[B] = \frac{K[A]_o}{K+1}\left(1-e^{-(k_1+k_2)t}\right) \qquad \ldots(25)$$

$$\text{Therefore,} \quad \frac{[B]}{[A]_o} = \frac{K}{K+1}\left(1-e^{-(k_1+k_2)t}\right) \qquad \ldots(26)$$

It can be observed that at t = 0, equation (26) becomes –

$$\frac{[B]}{[A]_o} \approx 0 \qquad \ldots(27)$$

and at t = ∞

$$\frac{[B]}{[A]_o} \approx \frac{K}{K+1} \qquad \ldots(28)$$

These can be graphically illustrated thus:

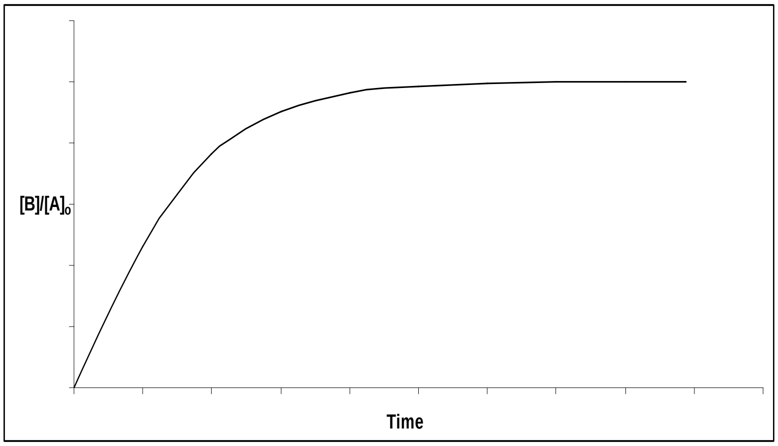

Fig. 2: Variation of $\frac{[B]}{[A]_o}$ with time

At large enough time (t = ∞), as equation (28) reveals, $\frac{[B]}{[A]_o}$ versus time plot becomes $\frac{K}{K+1}$.

Also Nnooa constant (K) can be estimated fom this plot. The fact that $\frac{[A]}{[A]_o}$ cannot be zero, as can be seen in Fig. 1, implies that $\frac{[B]}{[A]_o} \approx \frac{K}{K+1}$ at t = ∞ cannot be 1, also as revealed in Fig. 2.

CONCLUSION

The results of the foregoing sections lead to the following conclusions:

(i) The present and past linear forms of the solution to reversible first order reaction equation may not yield the same results. This is because, they are not the same expression and a work[6] demonstrated that different linear expressions do not yield the same results from their plots.

(ii) The past solution expressions do not contain the equilibrium constant in the expressions but the present ones do, hence, determination of Nnooa constant (K) from $[A]/[A]_o$ and $[B]/[A]_o$ versus time plots can be done.

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