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Modeling of Sample Withdrawal Effects on Pseudo-Order Batch Sorption Kinetics

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Abstract – Apparent sorption kinetics determined from single-run batch studies can drift significantly from true kinetics in systems where sorbent quantity remains constant with respect to sample withdrawal. This systematic error is investigated for sorption reaction models, generalized to any reaction order. The problem is formulated to quantify the bias associated with the number and volume of samples withdrawn under relatively slow equilibrium. The results are extended to rapidly equilibrating systems following the Langmuir isotherm model.

Keywords – pseudo-order, sorption, kinetics, equilibrium, modeling, bias, sampling error

I. INTRODUCTION

Sorption is the process involving the assimilation of one substance into another, may it be by either or a combination of absorption and adsorption [1]. In the context of wastewater treatment applications, chemical species of interest are taken out of solution by their incorporation into a solid called a sorbent, which is either disposed of or treated afterwards to recover the incorporated species called sorbate and regenerate the spent sorbent.

Part of characterizing sorbents is determining the kinetic and equilibrium behavior of the sorbate-sorbent system by sorption studies. Batch kinetic studies are typically carried out by periodically taking aliquots of the solution, which has been contacted with the sorbent under stirred conditions, for analysis; the points collected can also serve to determine when the equilibrium time has been reached in the construction of equilibrium curves if the equilibrium time is not taken to be 24h or longer [2]–[10]. In all these studies, a suitable model is chosen to obtain a mathematical description useful for process design. Throughout the years, several models have been proposed and applied to a variety of sorbate-sorbent systems [11]–[17].

An interesting question is the kinetic consequences of only sampling the solution and none of the sorbent, as it is conceivable that this systematic alteration of the solution-to-sorbent ratio would influence the tendency of the sorbate to apportion itself across the solution and sorbent phases by varying the relative amount of each. In order to examine this idea, the pseudo-second order equation was chosen given that it is one of the most commonly employed mathematical expressions to describe sorption processes due to its wide applicability [18], [19].

Besides pseudo-second order, other pseudo-ordered models and combinations have appeared in literature. Langmuir kinetics has been shown to be the sum of pseudo-first and pseudo-second order terms which simplifies to either pseudo-first or pseudo-second under an appropriate set of conditions

[20], [21]. A general pseudo-order form has also been proposed and utilized in modeling sorption kinetics [22]– [25].

This paper presents a mathematical evaluation of the systematic bias associated with sample withdrawal for sorption systems following the pseudo-second order model. These results are then generalized to any reaction order. As pseudo-ordered models are functions of the equilibrium concentration, another consequence of sample withdrawal is an additional bias brought about by possible perturbations in the equilibrium concentration — this effect is also examined for the case modeled by the Langmuir isotherm for sorption equilibrium.

II. MODELING

2.1 Effect of Sample Withdrawal

2.1.1 Pseudo-second order kinetics

In batch systems where analyte measurement involves the collection of only the solution and none of the sorbent material, each sample withdrawal can be conceived to impose a systematic error by perturbation of the system's kinetics.

To mathematically describe the effect of sample collection on the sorbate concentration in the remaining solution, the following assumptions are made:

1. Sorption kinetics is modeled by a pseudo-second order equation based on solid phase sorption:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

where qe and qt are the amount of solute sorbed per weight of sorbent at equilibrium and at time t respectively, and k is the rate constant.

2. The amount of sorbent in the solution remains constant.
3. The rate constant is a function of temperature only.
4. Sorption proceeds isothermally.
5. Perturbations do not significantly alter the initial equilibrium state, i.e., the equilibrium concentration can be considered practically invariant with respect to changes in solution volume.

A chemical species balance for the sorbate yields the following relation

$$C_0V = C_tV + q_tW = C_eV + q_eW \tag{2}$$

where C_0, C_t, C_e are the solute concentrations initially, at time *t*, and at equilibrium respectively; *V* is the volume of the solution; and W is the weight of the sorbent.

Substitution of Eq. (2) into Eq. (1) gives

$$\frac{dC_t}{dt} = -k\left(\frac{V}{W}\right)(C_t - C_e)^2 \tag{3}$$

The solution of differential Eq. (3) is

$$\frac{1}{C_f - C_e} - \frac{1}{C_i - C_e} = k\left(\frac{V}{W}\right)(t_f - t_i) \tag{4}$$

where the subscripts i and f indicate the initial and final quantities respectively.

Equation (4) describes the change in concentration over time under constant solution volume; however, sample withdrawal of only the solution will vary V in the V/W term. Thus, to account for the changes in volume, Eq. (4) is rewritten as

$$\frac{1}{C_j - C_e} - \frac{1}{C_{j-1} - C_e} = k\left(\frac{V_{j-1}}{W}\right)(t_j - t_{j-1}) \tag{5}$$

where C_j, t_j, and V_j represents the concentration, time, and the remaining solution volume upon drawing off the jth sample respectively.

Summing Eq. (5) over all samples withdrawn, i.e. $j = 1$ to n, yields

$$\frac{1}{C_n - C_e} - \frac{1}{C_0 - C_e} = \frac{k}{W}\left[V_{n-1}t_n - V_0 t_0 + \sum_{j=1}^{n-1}(V_{j-1} - V_j)t_j\right] \tag{6}$$

If samples are withdrawn in equal volumes , i.e. $V_{j-1} - V_j = -\Delta V$, Eq. (6) becomes

$$\frac{1}{C_n - C_e} - \frac{1}{C_0 - C_e} = \frac{k}{W}\left[V_{n-1}t_n - V_0 t_0 + (-\Delta V)\sum_{j=1}^{n-1} t_j\right] \tag{7}$$

Since, for $n \geq 2$, $V_{n-1} = V_0 - (n-1)(-\Delta V)$, and taking $t_0 = 0$, Eq. (7) can be expressed as

$$\frac{1}{C_n - C_e} - \frac{1}{C_0 - C_e} = \frac{k}{W}\left\{V_0 t_n + (-\Delta V)\left[\sum_{j=1}^{n-1} t_j - (n-1)t_n\right]\right\} \tag{8}$$

On the other hand, considering the ideal case of in situ measurements made at constant solution volume for the same system, the change in concentration with respect to time is simply

$$\frac{1}{C_t - C_e} - \frac{1}{C_0 - C_e} = k\left(\frac{V_0}{W}\right)t_n \tag{9}$$

where C_t is the concentration at the time corresponding to taking an nth sample from the prior case, t_n, described in Eqs. (6) to (8).

To determine the departure in the concentration due to sample withdrawal with respect to this in situ case, the ratio of Eqs. (8) and (9) are reduced to

$$\frac{(C_t - C_n)(C_0 - C_e)}{(C_0 - C_t)(C_n - C_e)} = \frac{(-\Delta V)}{V_0}\left[\frac{1}{t_n}\sum_{j=1}^{n-1} t_j - (n-1)\right] \tag{10}$$

Since $(1/t_n)\sum_{j=1}^{n-1} t_j < n - 1$, for $n \geq 2$, Eq. (10) expressed in terms of only positive quantities is

$$\frac{(C_n - C_t)(C_0 - C_e)}{(C_0 - C_t)(C_n - C_e)} = \frac{(-\Delta V)}{V_0}\left[n - 1 - \frac{1}{t_n}\sum_{j=1}^{n-1} t_j\right] \tag{11}$$

which implies that $C_0 > C_n > C_t > C_e$; the effect of sample withdrawal is to cause the sorbate concentration to be higher than the ideal case.

Equation (11) can be rearranged into the following form

$$\frac{1}{C_n - C_e} = \frac{\alpha}{C_t - C_e} + \frac{1-\alpha}{C_0 - C_e} \tag{12}$$

where

$$\alpha = 1 - \frac{(-\Delta V)}{V_0}\left[n - 1 - \frac{1}{t_n}\sum_{j=1}^{n-1} t_j\right], \quad \text{for } n \geq 2 \tag{13}$$

The value of 1 − α can be seen as a product of the relative sample volume, $(-\Delta V)/V_0$, and a sampling frequency term,. If the time intervals between sample withdrawals are the same, Eq. (13) can be simplified into

$$\alpha = 1 - \frac{(-\Delta V)}{V_0}\left(\frac{n-1}{2}\right), \quad \text{for } n \geq 1 \tag{14}$$

Based on Eq. (12) with α constant, *as* $C_t \rightarrow C_e$, $C_n \rightarrow C_e$ implying that $C_t = C_n$ at equilibrium. It can also be shown for the trivial case of $C_t = C_0$ that $C_n = C_t$. Therefore, it follows that $C_n - C_t = 0$ for both initial and equilibrium states; hence, a maximum $C_n - C_t$ exists between C_0 and C_e. Furthermore, following this argument, together with Eqs. (11) and (13), it must be that $0 \leq \alpha \leq 1$.

Rewriting Eq. (12) as

$$C_n - C_t = \frac{1}{\dfrac{\alpha}{C_t - C_e} + \dfrac{1-\alpha}{C_0 - C_e}} - (C_t - C_e) \tag{15}$$

the value of $C_n - C_t$ is found to be maximum at

$$\underset{C_t}{\arg\max}(C_n - C_t) = C_e + \frac{\sqrt{\alpha}}{1+\sqrt{\alpha}}(C_0 - C_e) \tag{16}$$

Substitution of Eq. (16) into Eq. (15) yields

$$\max(C_n - C_t) = \frac{1-\sqrt{\alpha}}{1+\sqrt{\alpha}}(C_0 - C_e) \tag{17}$$

Equation (17) indicates that any combination of high C_0, low C_e, and large changes in solution volume will increase the discrepancy between C_n and C_t.

If rendered in dimensionless form, Eq. (12) becomes

$$\chi = \frac{1}{\alpha/\psi + 1 - \alpha} - \psi \tag{18}$$

defined by dimensionless ratios

$$\chi = (C_n - C_t)/(C_0 - C_e) \tag{19}$$

$$\psi = (C_t - C_e)/(C_0 - C_e) \tag{20}$$

where χ and ψ can be interpreted as the relative concentration drift and the relative unaccomplished concentration change in the in situ case respectively.

Combining Eq. (9) with the definition of ψ in Eq. (18) at a fixed sampling time interval, Δt, yields

$$\psi = \frac{1}{1 + (\Delta t/\tau)n} \tag{21}$$

with a characteristic time

$$\tau = \frac{1}{k(V_0/W)(C_0 - C_e)}$$

Given that the maximum number of samples that can be withdrawn is

$$n_{\max} = V_0/(-\Delta V) \tag{22}$$

the α value from Eq. (14) upon withdrawal of the last sample can be rewritten as

$$\alpha = 1 - \frac{n-1}{2n_{\max}} \tag{23}$$

showing α in relation to the unsampled fraction of the system. This result indicates that α cannot have a value lower than 0.5 which, upon substitution into Eq. (17), determines a relative drift χ not exceeding 0.17.

2.1.2 Pseudo-first-order kinetics

Replacing Eq. (1) with

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{24}$$

results to Eq. (3) becoming

$$\frac{dC_t}{dt} = -k(C_t - C_e) \tag{25}$$

The absence of *V /W* implies pseudo-first-order kinetics is invariant with shifts in the ratio between solution volume and adsorbent weight.

2.1.3 Generalized pseudo-order kinetics

Viewing pseudo-first and pseudo-second-order kinetics as special cases of

$$\frac{dq_t}{dt} = k(q_e - q_t)^x \tag{26}$$

following the same steps done for pseudo-second-order kinetics at $t_0 = 0$ yields

$$(C_n - C_e)^{1-x} - (C_0 - C_e)^{1-x} = (x-1)\frac{k}{W}\left[V_{n-1}^{x-1}t_n + (-\Delta V)^{x-1}\sum_{j=1}^{n-1} t_j\right] \tag{27}$$

and

$$(C_t - C_e)^{1-x} - (C_0 - C_e)^{1-x} = (x-1)\frac{k}{W}V_0^{x-1}t_n \tag{28}$$

for sampled and ideal cases respectively.

Taking the ratio of Eqs. (27) and (28) yields

$$\frac{(C_n - C_e)^{1-x} - (C_0 - C_e)^{1-x}}{(C_t - C_e)^{1-x} - (C_0 - C_e)^{1-x}} = \left[\left(\frac{V_{n-1}}{V_0}\right)^{x-1} + \left(\frac{-\Delta V}{V_0}\right)^{x-1}\frac{1}{t_n}\sum_{j=1}^{n-1} t_j\right] \tag{29}$$

which upon subtraction from one on both sides of the equation gives

$$\frac{(C_t - C_e)^{1-x} - (C_n - C_e)^{1-x}}{(C_t - C_e)^{1-x} - (C_0 - C_e)^{1-x}} = 1 - \left[\left(\frac{V_{n-1}}{V_0}\right)^{x-1} + \left(\frac{-\Delta V}{V_0}\right)^{x-1}\frac{1}{t_n}\sum_{j=1}^{n-1} t_j\right] \tag{30}$$

If samples are withdrawn at constant time interval and volume and substituting into Eq. (22), Eq. (30) becomes

$$\frac{(C_t - C_e)^{1-x} - (C_n - C_e)^{1-x}}{(C_t - C_e)^{1-x} - (C_0 - C_e)^{1-x}} = 1 - \left[\left(1 - \frac{n-1}{n_{\max}}\right)^{x-1} + \frac{n-1}{2n_{\max}^{x-1}}\right] \tag{31}$$

Going back through Eqs. (29) to (31), the right-hand side of Eq. (29) must be α; thus, from the left-hand side of this equation, α can be thought of as a kinetic coefficient describing the performance of the sampled system relative to its ideal unperturbed counterpart.

It can be shown that when $x = 2$, the right-hand side of Eq. (31) reduces to Eq. (23); thus, the generalized form of α is

$$\alpha = \left(1 - \frac{n-1}{n_{\max}}\right)^{x-1} + \frac{n-1}{2n_{\max}^{x-1}} \tag{32}$$

Looking at the left-hand side of Eq. (31), it follows that $C_n > C_t$ when $\alpha < 1$ and $C_n < C_t$ when $\alpha > 1$ for any reaction order $x \neq 1$. Based on Eq. (32), α is shown to be nonnegative for any x. Accordingly,

$$\lim_{n \to n_{\max}} \alpha = \frac{n_{\max} + 1}{2n_{\max}^{x-1}} \tag{33}$$

When $x = 2$, Eq. (33) has a limiting α value of 0.5 as $n_{\max} \to +\infty$, consistent with the result from Eq. (23). This result appears special to pseudo-second-order kinetics as Eq. (33) remains bounded but at a lower value not exceeding 0 for $x > 2$ while the opposite occurs when $x < 2$ yielding α values that grow indefinitely with increasing $n_{\max}$.

Since $\alpha = 1$ when $n = 1$ for any x, the initial slope of Eq. (32) can determine whether the systematic error in the sampled system will be greater than or less than that of its ideal *in situ* counterpart.

Examination of the initial slope of α with respect to the number of samples withdrawn n

$$\left.\frac{\partial \alpha}{\partial n}\right|_{n=1} = \frac{1}{n_{\max}}\left(1 - x + \frac{1}{2n_{\max}^{x-2}}\right) \tag{34}$$

indicates that the initial slope is always negative when while x ≤ 1.5 would give a nonnegative slope, given that $n_{max} \geq 1$. For $1.5 < x < 2$, the initial slope is either positive or negative depending on the value of n_{max} .

Interestingly, Eq. (12) generalizes to

$$\frac{1}{(C_n - C_e)^{x-1}} = \frac{\alpha}{(C_t - C_e)^{x-1}} + \frac{1-\alpha}{(C_0 - C_e)^{x-1}} \tag{35}$$

from which all the other derivations as done for pseudo-second-order follows after. Thus, Eqs. (15) to (17) generalized to any reaction order x becomes

$$C_n - C_t = \frac{1}{\left[\dfrac{\alpha}{(C_t - C_e)^{x-1}} + \dfrac{1-\alpha}{(C_0 - C_e)^{x-1}}\right]^{\frac{1}{x-1}}} - (C_t - C_e) \tag{36}$$

$$\operatorname*{arg\,max}_{C_t}(C_n - C_t) = C_e + \alpha^{\frac{1}{x}} \left(\frac{1-\alpha^{\frac{1}{x}}}{1-\alpha}\right)^{\frac{1}{x-1}} (C_0 - C_e) \tag{37}$$

$$\max(C_n - C_t) = (1 - \alpha^{\frac{1}{x}}) \left(\frac{1-\alpha^{\frac{1}{x}}}{1-\alpha}\right)^{\frac{1}{x-1}} (C_0 - C_e) \tag{38}$$

Likewise, using dimensionless ratios in Eq. (19) defined for the pseudo-second-order case χ and ψ, the following are obtained for the generalized case

$$\chi = \frac{1}{(\alpha/\psi^{x-1} + 1 - \alpha)^{\frac{1}{x-1}}} - \psi \tag{39}$$

$$\psi = \frac{1}{[1 + (\Delta t/\tau)n]^{\frac{1}{x-1}}} \tag{40}$$

$$\tau = \frac{1}{(x-1)k(V_0^{x-1}/W)(C_0 - C_e)^{x-1}} \tag{41}$$

It must be pointed out from Eq. (41) that, for values of $x < 1$, (*a*) τ becomes negative which in turn based on Eq. (40) results to (*b*) ψ approaching 0 at finite time, examination of Eq. (33) reveals that (*c*) α can easily become large as $n \rightarrow n_{max}$ and given these last two observations, as seen in Eq. (39), (*d*) χ tends to negative infinity but only if x is an even number.

2.1.4 Pseudo-order kinetics with reactions orders of less than one

Due to the peculiarity that ψ approaches 0 at finite time due to $\tau < 0$, the relevant time interval for sorption systems described by kinetics of order $x < 1$ to be sampled is before the process ceases, which based on Eq. (40) would be $n\Delta t/(-\tau) < 1$. This behavior puts a cap on the total number of samples that can be drawn in the ideal in situ case, which is $n_{max} = (-\tau)/\Delta t$. However, $C_n < C_t$ when $\alpha > 1$ which is the case for reaction orders $x < 1$. Thus, the sampled system will reach equilibrium first before its ideal in situ counterpart.

To establish the point in the process where sorption in the sampled system ceases, it is recognized that this state corresponds to $C_n = C_e$ or, in terms of dimensionless variables, $\chi = -\psi$. Substitution into Eq. (39) implies that the α-containing term must be zero; in other words, the reaction runs from $\psi = 1$ to

$$\psi = \left(1 - \frac{1}{\alpha}\right)^{\frac{1}{1-x}} \tag{42}$$

which provides a relation that determines what fraction of nmax in the ideal in situ system can only be realized in its sampled counterpart before it terminates. Expanding Eq. (42) in terms of n and designating $\theta = n/n_{max}$,

$$\frac{1}{\theta} = \frac{1}{\left(1 + \dfrac{1}{n_{\max}} - \theta\right)^{1-x}} + \frac{n_{\max}^{2-x}}{2}\left(\theta - \frac{1}{n_{\max}}\right), \qquad x < 1 \tag{43}$$

which shows that this limit will vary with the total number of samples that can be withdrawn in the ideal in situ case n_{max} and reaction order x.

Making order-of-magnitude arguments, when $n_{\max}$ is large, Eq. (43) becomes

$$\frac{1}{\theta} \approx \frac{1}{(1-\theta)^{1-x}} + \frac{n_{\max}^{2-x}\,\theta}{2}, \qquad x < 1 \tag{44}$$

which can be rearranged to

$$\frac{2\theta}{2 - n_{\max}^{2-x}\,\theta^2} \approx (1-\theta)^{1-x}, \qquad x < 1 \tag{45}$$

Since the right-hand side of Eq. (45) indicates no discontinuities and positive values only for $0 \leq \theta \leq 1$, the denominator of the left-hand side must always be greater than zero, i.e.,

$$\theta \lesssim \left(\frac{2}{n_{\max}^{2-x}}\right)^{\frac{1}{2}}, \qquad x < 1 \tag{46}$$

From this approximation, Eq. (46) indicates that the θ value corresponding to the completion of the reaction in the sampled system is inversely proportional to $n_{\max}^{1-\frac{x}{2}}$. Thus, both an increase in $n_{\max}$ and decrease in x would result to a diminishing fraction of $n_{\max}$ that can be drawn and a consequently narrower range of ψ values from initial state to equilibrium.

2.2 Perturbations in Equilibrium Concentration

The equations derived in the previous section hold provided the equilibrium concentration, C_e, remains practically the same throughout sample withdrawals. To quantitate this assumption, an analysis limited to sorption equilibrium following the Langmuir isotherm

$$q_e = Q\frac{KC_e}{1+KC_e} \tag{47}$$

is made, where q_e is the equilibrium amount of solute sorbed per weight of sorbent, Q is the maximum amount of solute sorbed per weight of sorbent, C_e is the equilibrium solute concentration in the solution, and K is the Langmuir sorption coefficient. This choice is driven by its amenability to an analytical solution.

When Eq.(47) is combined with Eq.(2) to eliminate qe, the value of C_e can be determined from the resulting equation to be

$$C_e = \frac{C}{2} + \sqrt{\left(\frac{C}{2}\right)^2 + \frac{C_0}{K}} \tag{48}$$

where $C = C_0 - 1/K - WQ/V$.

In differential form, Eq. (48) becomes

$$dC_e = \frac{1}{2}\frac{WQ}{V}\frac{dV}{V}\left[1 + \frac{\frac{C}{2}}{\sqrt{\left(\frac{C}{2}\right)^2 + \frac{C_0}{K}}}\right] \tag{49}$$

Since

$$\frac{C}{2} \leq \sqrt{\left(\frac{C}{2}\right)^2 + \frac{C_0}{K}} \tag{50}$$

It follows that

$$\frac{1}{2}\frac{WQ}{V}\frac{dV}{V} \leq dC_e \leq \frac{WQ}{V}\frac{dV}{V} \tag{51}$$

Equation (51) indicates that the perturbation in equilibrium concentration, dC_e, depends on the maximum amount of sorbable solute per volume of solution, WQ/V , and the relative volume change, dV/V . It also shows that sample withdrawals decrease the equilibrium concentration in the solution for systems following Langmuir sorption model.

2.3 Effect of shifting equilibrium during sample withdrawal

In deriving either Eq. (6) or Eq. (27), it is assumed that the equilibrium concentration C_e is constant even though, from Eq. (51), it should decrease with decreasing volume for Langmuir sorption. This condition of constant C_e may be thought to correspond to a relatively slow shift towards the new equilibrium state in response to sample withdrawal or the final equilibrium state itself after shifting is small as to make it practically constant. However, if on the other end the system should rapidly adjust towards a significantly different equilibrium state after each sampling, then the sorbate concentration in solution in this case will deviate from the constant C_e case in response to this equilibrium concentration change. By taking these changes in C_e to be instantaneous, the sorption rate at the beginning of a sampling interval is at its largest and thus the maximum deviation from the constant C_e case can be determined. At each sampling interval, both cases are related to each other by the equation

$$(C_{j,0} - C_{e,0})^{1-x} - (C_{j-1,0} - C_{e,0})^{1-x} = (C_{j,j-1} - C_{e,j-1})^{1-x} - (C_{j-1,j-1} - C_{e,j-1})^{1-x}$$
$$= (x-1)k\left(\frac{V_{j-1}}{W}\right)(t_j - t_{j-1}), \quad \text{for } j \geq 1 \qquad (52)$$

where a second subscript is introduced in the notation to indicate the sampling interval the concentrations are referenced to, with the first sampling interval designated as 0; the equilibrium concentration in the constant C_e case is fixed to that at the initial equilibrium state and thus designated by a second subscript assignment of 0. As a consequence of this notation, it should be noted that *Cj,j* = $C_{j,j-1}$ as both terms refer to the same sorbate concentration in solution albeit referenced to different equilibrium concentrations.

Carrying out the same procedure for deriving Eq. (6) or its generalized analog Eq. (27), Eq. (52) becomes

$$(C_{n,0} - C_{e,0})^{1-x} - (C_0 - C_{e,0})^{1-x} =$$
$$(C_{n,n-1} - C_{e,n-1})^{1-x} - (C_0 - C_{e,0})^{1-x} + \sum_{j=1}^{n-1}(C_{j,j-1} - C_{e,j-1})^{1-x} - (C_{j,j-1} - C_{e,j})^{1-x}$$
$$= (x-1)\frac{k}{W}\left[V_{n-1}^{x-1}t_n + (-\Delta V)^{x-1}\sum_{j=1}^{n-1} t_j\right] \qquad (53)$$

where summing over all samples in the perturbed C_e case — unlike in the constant C_e case — will not cancel out the intermediate concentration terms due to differences in C_e before and after each sample withdrawal.

Keeping only the concentration terms in Eq. (53) and simplifying gives

$$(C_{n,0} - C_{e,0})^{1-x} = (C_{n,n-1} - C_{e,n-1})^{1-x} + \sum_{j=1}^{n-1}(C_{j,j-1} - C_{e,j-1})^{1-x} - (C_{j,j-1} - C_{e,j})^{1-x} \qquad (54)$$

For the case of $x = 1$, it can be shown that

$$\ln(C_{n,0} - C_{e,0}) = \ln(C_{n,n-1} - C_{e,n-1}) + \sum_{j=1}^{n-1}\ln(C_{j,j-1} - C_{e,j-1}) - \ln(C_{j,j-1} - C_{e,j}) \qquad (55)$$

Since from Eq. (51) $C_{e,j} < C_{e,j-1}$ for Langmuir sorption, it follows that

$$(C_{j,j-1} - C_{e,j-1})^{1-x} - (C_{j,j-1} - C_{e,j})^{1-x} > 0 \qquad \text{when } x > 1 \qquad (56)$$

$$\ln(C_{j,j-1} - C_{e,j-1}) - \ln(C_{j,j-1} - C_{e,j}) < 0 \qquad \text{when } x = 1 \qquad (57)$$

$$(C_{j,j-1} - C_{e,j-1})^{1-x} - (C_{j,j-1} - C_{e,j})^{1-x} < 0 \qquad \text{when } x < 1 \qquad (58)$$

$$0 \leq C_{n,0} - C_{e,0} \leq C_{n,n-1} - C_{e,n-1} \qquad \text{for all } x \qquad (59)$$

Divergence in the kinetics of the two cases begins after the first sampling interval. At $j = 2$, Eq. (52)

can be written off as

$$(C_{2,0} - C_{e,0})^{1-x} - (C_{1,0} - C_{e,0})^{1-x} = (C_{2,1} - C_{e,1})^{1-x} - (C_{1,1} - C_{e,1})^{1-x} \tag{60}$$

With Eq. (59), it can be shown from the time derivatives of Eq. (60) that

$$\frac{dC_{2,0}/dt}{dC_{2,1}/dt} = \left(\frac{C_{2,0} - C_{e,0}}{C_{2,1} - C_{e,1}}\right)^x \leq 1 \qquad \text{when } x > 0 \tag{61}$$

$$\frac{dC_{2,0}/dt}{dC_{2,1}/dt} = \left(\frac{C_{2,0} - C_{e,0}}{C_{2,1} - C_{e,1}}\right)^x \geq 1 \qquad \text{when } x < 0 \tag{62}$$

Therefore, with $C(t)$ monotonic at any point within $t_1 \leq t \leq t_2$, the sorption rate is slower/faster in the constant C_e case relative to perturbed for positive/negative reaction orders x; since $dC/dt < 0$, the sorbate concentration in solution for the constant C_e case must consequently be higher/lower. Likewise, for any sampling interval

$$\frac{dC_{j,0}/dt}{dC_{j,j-1}/dt} = \left(\frac{C_{j,0} - C_{e,0}}{C_{j,j-1} - C_{e,j-1}}\right)^x \leq 1 \qquad \text{when } x > 0 \tag{63}$$

$$\frac{dC_{j,0}/dt}{dC_{j,j-1}/dt} = \left(\frac{C_{j,0} - C_{e,0}}{C_{j,j-1} - C_{e,j-1}}\right)^x \geq 1 \qquad \text{when } x < 0 \tag{64}$$

Hence

$$C_{j,j-1} \leq C_{j,0} \qquad \text{when } x > 0 \tag{65}$$

$$C_{j,j-1} \geq C_{j,0} \qquad \text{when } x < 0 \tag{66}$$

Combining Eqs. (65) and (66) with Eq. (59) results to

$$C_{n,0} - (C_{e,0} - C_{e,n-1}) \leq C_{n,n-1} \leq C_{n,0} \qquad \text{when } x > 0 \tag{67}$$

$$C_{n,0} \leq C_{n,n-1} \qquad \text{when } x < 0 \tag{68}$$

having both upper and lower bounds possible only with Eq. (67).

In dimensionless form, Eqs. (67) and (68) becomes

$$\chi_0 - \kappa \leq \chi_{n-1} \leq \chi_0 \qquad \text{when } x > 0 \tag{69}$$

$$\chi_0 \leq \chi_{n-1} \qquad \text{when } x < 0 \tag{70}$$

respectively, where

$$\chi_j = (C_{n,j} - C_t)/(C_0 - C_{e,0})$$
$$\kappa = (C_{e,0} - C_{e,n-1})/(C_0 - C_{e,0})$$

For completeness, reaction order $x = 0$ behaves independently of concentration and as such do not deviate with changes in C_e.

III. DISCUSSION OF RESULTS

The relationship between bias χ, reaction coordinate ψ, and α is illustrated for the pseudo-second order case in Fig. 1: concave lines of constant α with a maximum given by Eqs. (16) and (17). As α is an index of the departure in the kinetics of the sampled system with respect to the *in situ* system, these α reaction trajectories originate from the x-axis ($\chi = 0$) and propagate in the direction of increasing bias ($\chi \rightarrow 1$) with each sampling. The concavity arises from the slower kinetics of the sampled system relative to its *in situ* counterpart, which leads to the initial rise in the reaction trajectories; however, as a consequence of the *in situ* system approaching equilibrium faster, the *in situ* case at some point slows down thus allowing the sampled system's kinetics to catch up, resulting in the downward dip of the curve. The diagonal represents the case where $C_n = C_0$; hence, all the states possible for pseudo-second order lies in the triangular region bounded by this diagonal with respect to the axes.

All reactions initially lie on $\alpha = 1$ ($\chi = 0$), starting on the vertex at $\psi = 1$. The rate at which reactions traverse horizontally towards the vertex at $\psi = 0$ is governed by its characteristic time τ: the smaller the characteristic time, the faster the reaction travels toward $\psi = 0$ at a decelerating pace (Fig. 2). However, sample withdrawal pulls the reaction trajectory towards the vertex at $\chi = 1$, drawing it farther from $\chi = 0$ with each sampling. This behavior is illustrated for $\Delta t/\tau = 0.3$ where the reaction moves from right to left, with sampling tugging its trajectory upward (Fig. 2, *left*). More emphasis is placed on the points at sampling rather than on the reaction path itself and therefore reaction progress is delineated instead with traces joining the sampling points. Location of the sampling points with respect to the reaction trajectories' locus of maxima determines the concavity of the χ-n trend line (Fig. 2, *right*). From Eq. (23), the bias in the pseudo-second order case is always bounded with all sampling points falling below $\alpha = 0.5$; at full sampling of all of the reaction volume, the highest achievable possible bias for the case of $n_{\max} = 10$ is reached when $\Delta t/\tau = 0.1348$.

The limit of $\alpha = 0.5$ for pseudo-second order is found to be a special case and is not observed for other pseudo orders in general. A plot of Eq. (32) indicates this behavior as well as demonstrates the characteristics drawn from Eqs. (33) and (34) for other pseudo orders (Fig. 3). From the plot, reaction order $x = 1.75$ can be considered practically invariant in terms of α; reaction orders below it have α values decreasing toward zero while those above have their α values increasing (Fig. 3). For either side,

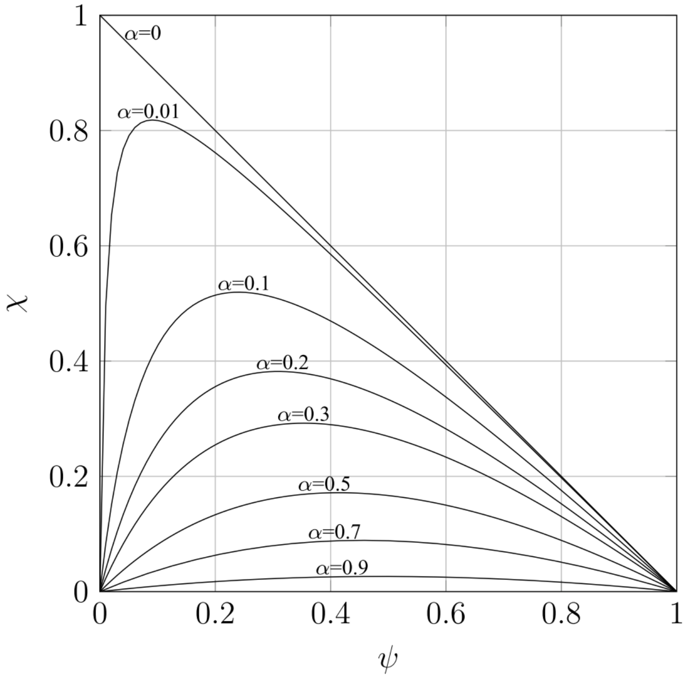

Figure 1. Relation of the relative concentration drift χ with respect to the relative unaccomplished concentration change in the *in situ* case ψ for various α values under pseudo-second-order kinetics.

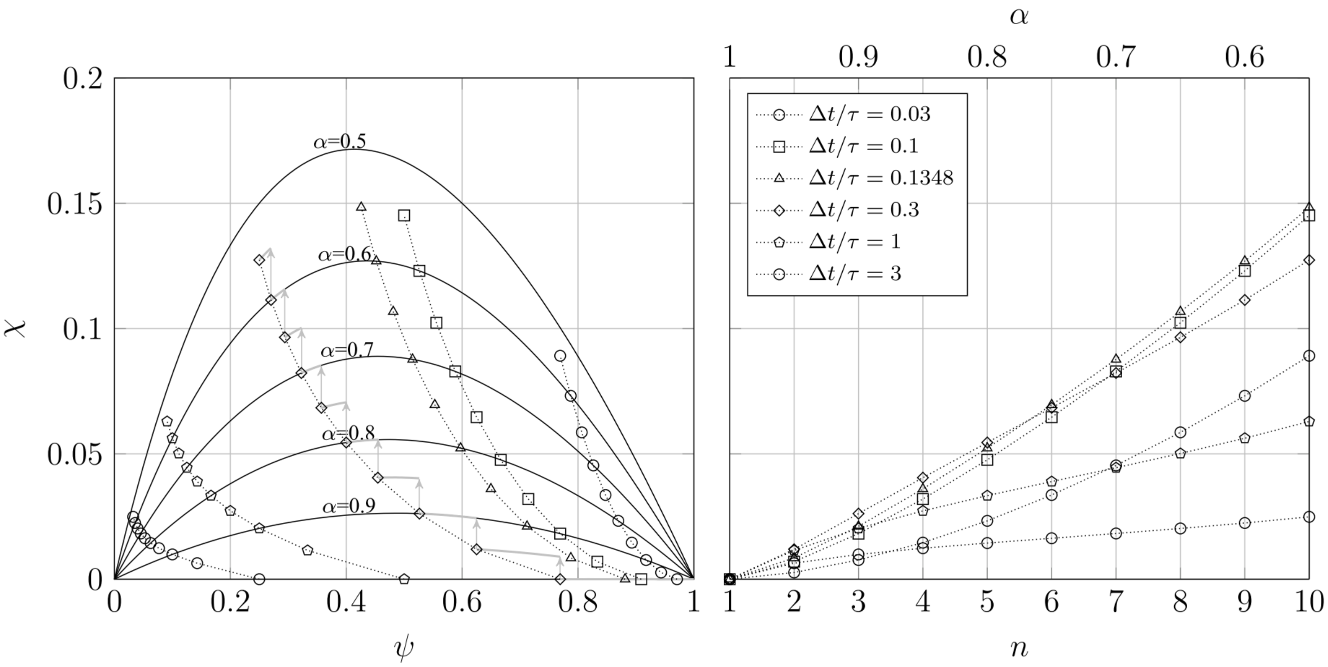

Figure 2. Characteristic curves with respect to $\Delta t/\tau$ for $n_{\max} = 10$ under pseudo-second-order kinetics. An illustration of a reaction trajectory (light gray lines with arrows) is drawn for $\Delta t/\tau = 0.3$.

the farther the departure of the reaction order from 1.75, the larger the change in α with respect to n. The plot also shows that $x = 1.75$ can cross $\chi = 0$ which is probably also the case for $1.5 \leq x \leq 2$.

If in pseudo-second order $0 \leq \alpha < 1$ corresponds to positive χ values, then $\alpha > 1$ should correspond to negative χ values, as it implies faster kinetics in the sampled system relative to its *in situ* counterpart. This point is illustrated in Fig. 4, using the reaction trajectories' loci of extrema to show that

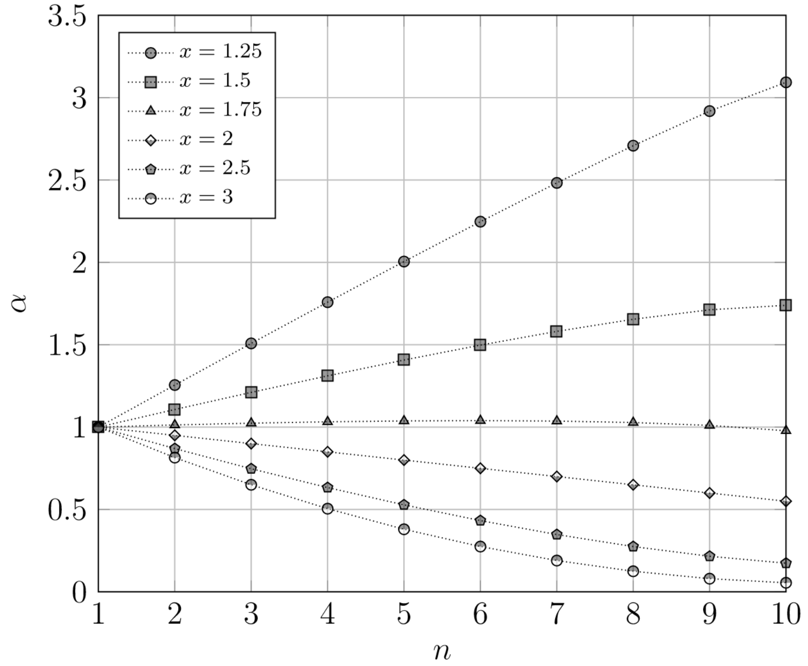

Figure 3. Behavior of α with respect to number of samples taken n at various reaction order x for $n_{\max} = 10$.

this behavior is indeed the case. Outside $1.5 < x < 2$, reaction trajectories are expected to lie on only one side of $\chi = 0$; all the same, α values dictate whether the initial reaction trajectory at $\chi = 0$ becomes positively or negatively biased in terms of χ. If the maximum bias occurs at $\chi = 1$ for $\alpha < 1$, then for $\alpha > 1$, magnitude-wise the largest bias must be same but opposite in sign at $\chi = -1$. Therefore, the loci of extrema delineate the manner by which the reaction trajectories propagate towards $|x| = 1$, with this propagation diminishing under increasing perturbation from sampling for either side of $\alpha = 1$, terminating at an α limit given by Eq. (33) (Fig. 4, *left*). However, unlike for $\alpha < 1$ where the reaction trajectories shift towards $\psi = 0$, $\alpha > 1$ results to trajectories that shift towards $\psi = 1$ (Fig. 4, *right*). Thus, it appears that reaction trajectories with $\alpha > 1$ propagates towards $(\psi,\chi) = (1,-1)$ similar to how trajectories with $\alpha < 1$ propagate towards $(\psi,\chi) = (0,1)$. Given this similarity, it can be shown that trajectories with $\alpha > 1$ are bounded by $\chi = -\psi$ in the same way trajectories with $\alpha < 1$ are bounded by $\chi = 1 - \psi$. Expressing this equation in terms of concentrations, it reduces to $C_n = C_e$, indicating that this line marks reaction equilibrium. Hence, the entire reaction space is a rhomboid region bound by the initial *in situ* reaction line $\psi = 1$, the equilibrium *in situ* reaction line $\psi = 0$, the initial sampled reaction line $\chi = 1 - \psi$, and the equilibrium sampled reaction line $\chi = -\psi$.

For reaction orders greater than one, a decrease in reaction order causes the sampling trace to occur much later and span lower values of ψ (Fig. 5). Switching to ψ^{x-1} shows that at the same time the largest bias magnitude-wise migrates from the last sample towards samples close to $\psi = 1$ for reaction orders with $\alpha > 1$ (Fig. 5, *left*). Additionally, the sampling trace appears to converge towards $(\psi,\chi) = (0,0)$ as the reaction order approaches one (Fig. 5, *right*). Thus, it appears that pseudo-first order reaction corresponds to a degenerate reaction path collapsing unto a single point on the $\psi - \chi$ plot.

Unlike reaction orders greater than one, reaction orders less than one terminate at finite time as indicated by Eqs. (40) and (41), with the reaction running up to $\psi = 0$. However, Eqs. (42) and (46) show that the sampled system reaches equilibrium before this point, which also puts a cap on the number of pre-equilibrium samples that can be withdrawn. These properties are illustrated in Fig. 6, where traces spanning a continuum of sampling points are drawn given the sparseness in pre-equilibrium sampling points. It should be pointed out that all these traces intersect the equilibrium sampled reaction line, then travel along this diagonal, eventually terminating at $\psi = 0$. An interesting point to make is how sampling accelerates the approach towards equilibrium of these reaction systems.

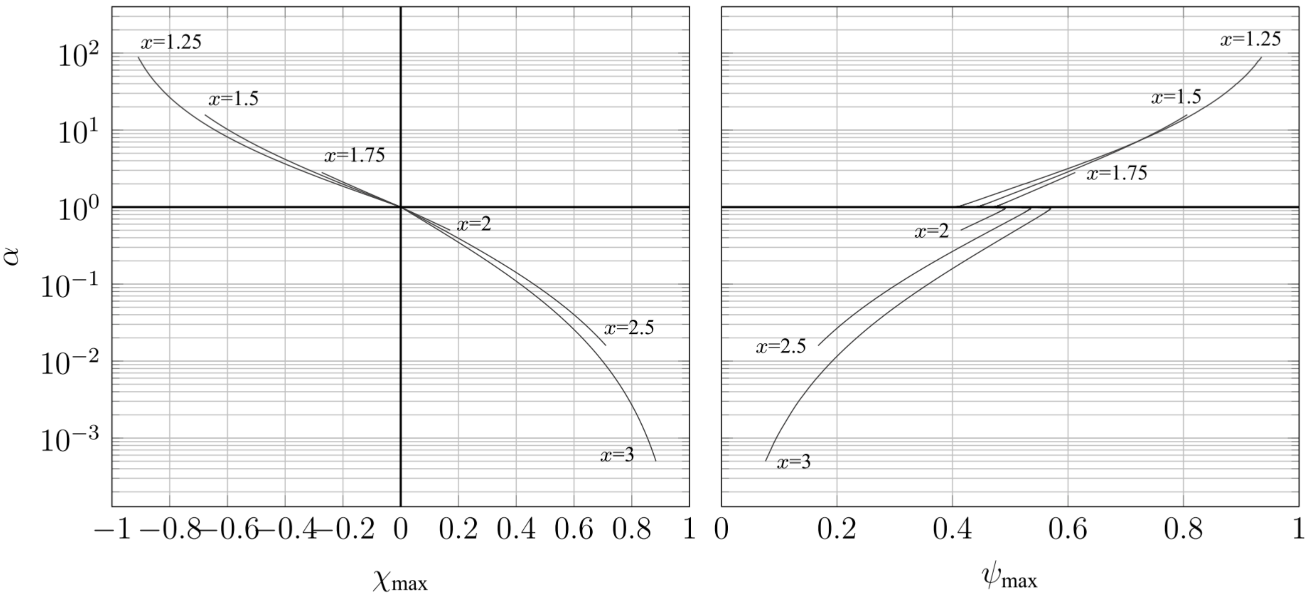

Figure 4. Loci of maxima from α trajectories from various reaction orders *x*, for samples withdrawn *n* ranging from 1 to $n_{\max} = 1000$ (points not shown).

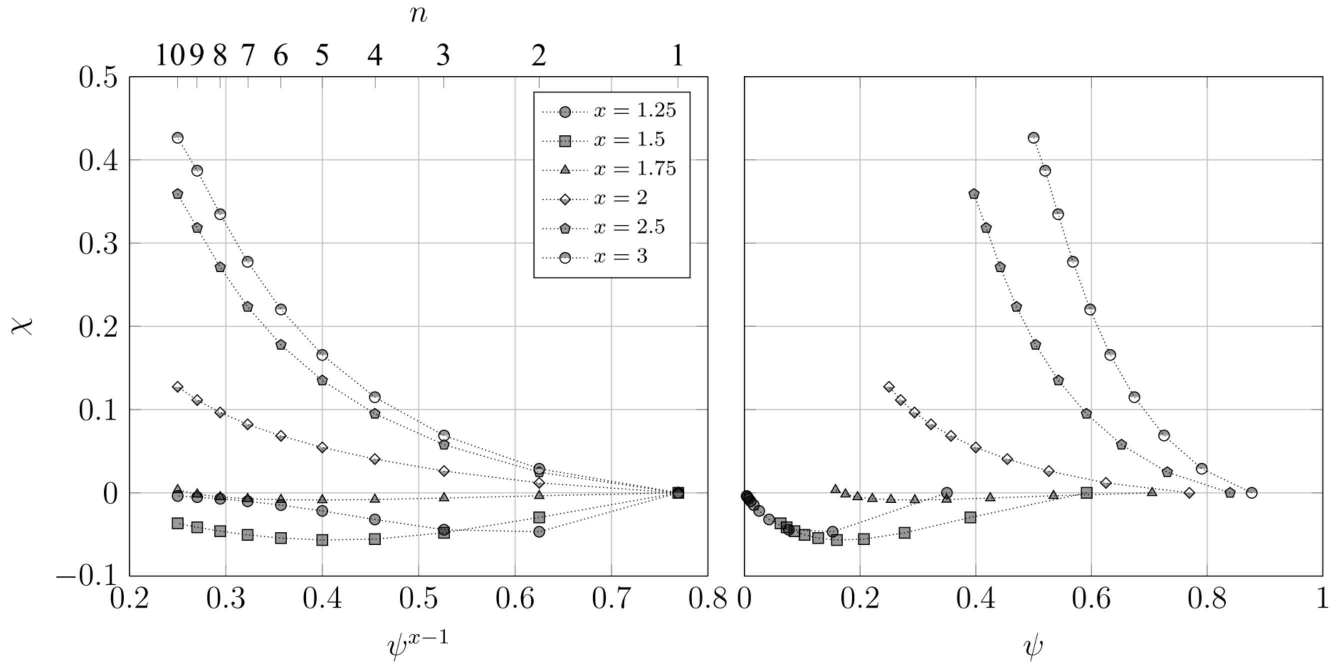

Figure 5. Behavior of χ with respect to number of samples taken *n* at various reaction orders $x > 1$ for $\Delta t/\tau = 0.3$ and $n_{\max} = 10$.

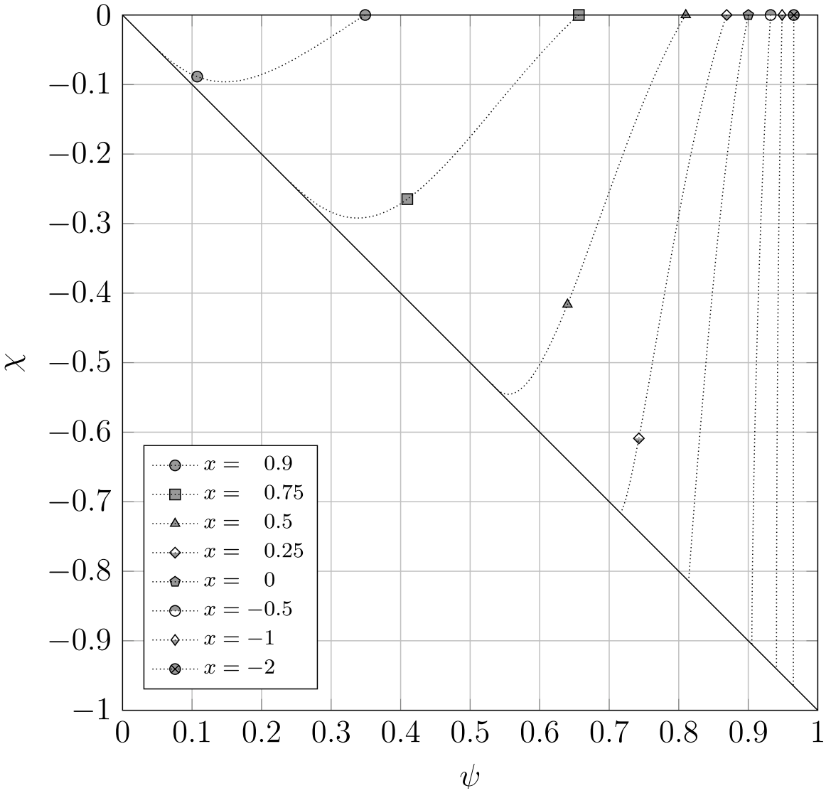

Figure 6. Characteristic curves at various reaction orders $x < 1$ for $n_{\max} = 10$. Reactions achieve equilibrium in finite time, depicted by the traces intersecting with the diagonal; only 1-2 points can be sampled prior to equilibrium, with rest lying on the diagonal (not drawn).

Finally, Eqs. (3), (24) and (55) reveal pseudo-first-order kinetics can be indirectly affected by sample withdrawal effects via perturbations in equilibrium concentration. Demonstrated for the case of Langmuir sorption, Eqs. (69) and (70) indicate that the reaction trajectories propagate to a lesser extent from $\chi = 0$ with decreasing equilibrium concentration. Interestingly, this behavior finds an exception for reaction orders $x > 0$ with $\alpha > 1$; in these cases, the opposite occurs where the negative bias is further decremented by the decreasing C_e, making the bias larger than that in the constant C_e case magnitude-wise. Zeroth pseudo-order kinetics are unaffected by changes in C_e.

IV. CONCLUSIONS AND RECOMMENDATIONS

This paper focused on the family of pseudo-ordered equations in evaluating the systematic bias associated with sample withdrawal. A dimensionless analysis of this problem yielded a mathematical framework for evaluating the extent by which these sampling-associated perturbations affect the quality of kinetic data collected under the assumption of intrinsic pseudo-ordered kinetics. It has been demonstrated that the source of the bias is twofold: variations in sorbent-solution ratios and perturbation in equilibrium concentration. Primarily, the kinetics of the sampled system being a function of its sorbent-to-solution ratio drives most of the systematic bias in pseudo-order kinetics with pseudo-first order as an exception. However, a secondary effect due to the equilibrium concentration also affecting the kinetics of the sampled system can further promote or suppress the propagation of this bias. Overall, the behavior of the systematic bias will depend on the interplay between the reaction order, characteristic time τ and the kinetic coefficient of performance α of the system.

The results of this work can be employed in several ways: In batch sorption experiments, a maximum acceptable bias can be established by specifying an α value to estimate the number of samples n of a given volume to be withdrawn out of the total number $n_{\max}$ that comprise the reaction volume for a chosen reaction order. This paper also provides an intriguing proposition of testing agreement to the pseudo-first order model by exhaustive sampling, deliberately modifying the sorbent-to-solution ratio to significant proportions to establish whether the reaction remains relatively insensitive to sampling (as pseudo-first order is still subject to perturbations in equilibrium concentration). From Eqs. (19), (32) and (40), it can be shown that the rearrangement of Eq. (39)

$$(\chi+\psi)^{1-x}-1=\alpha(\psi^{1-x}-1) \tag{71)}$$

expands to

$$\left(\frac{C_n-C_e}{C_0-C_e}\right)^{1-x}-1=\left(\frac{\Delta t}{\tau}\right)n\left[\left(1-\frac{n-1}{n_{\max}}\right)^{x-1}+\frac{n-1}{2n_{\max}^{x-1}}\right] \tag{72}$$

which is amenable to linear regression analysis for different assumed reaction orders, provided C_e is known; an increase in accuracy might be achieved when partnered with an appropriate equilibrium model if C_e may not be taken to be constant.

It should be pointed out that the findings presented in this paper are theoretical and remain to be demonstrated experimentally. Putting this point aside, it would be interesting to perform a similar analysis to other sorption kinetics models for insights that may be gained from how sampling bias would affect the kinetic behavior of systems governed by such models.

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Nomenclature

Dimensionless Numbers

Symbol	Description	Definition
α	reaction trajectory perturbation	$\left(1-\frac{n-1}{n_{\max}}\right)^{x-1}+\frac{n-1}{2n_{\max}^{x-1}}$
χ	relative concentration drift (constant equlibrium concentration case)	$(C_n-C_t)/(C_0-C_e)$
χ_j	relative concentration drift (shifting equlibrium concentration case)	$(C_{n,j}-C_t)/(C_0-C_{e,0})$
κ	relative equilibrium concentration drift	$(C_{e,0}-C_{e,n-1})/(C_0-C_{e,0})$
ψ	relative unaccomplished concentration change	$(C_t-C_e)/(C_0-C_e)$
τ	characteristic time	$\frac{1}{(x-1)k(V_0^{x-1}/W)(C_0-C_e)^{x-1}}$
θ	fraction of reaction volume sampled	$n/n_{\max}$

Greek Symbols

Symbol	Description	Dimensions
Δ	difference between two states	–

Roman Symbols

Symbol	Description	Dimensions
C	solute concentration	$[\mathrm{M/L^3}]$
K	Langmuir sorption coefficient	$[\mathrm{L^3/M}]$
k	rate constant	$[(\mathrm{M/M})^x/\mathrm{T}]$
n	total number of sample volumes withdrawn	[–]
$n_{\max}$	maximum number of sample volumes that can be withdrawn	[–]
Q	maximum amount of solute sorbed per weight of sorbent	[M/M]
q	amount of solute sorbed per weight of sorbent	[M/M]
t	reaction time	[T]
V	reaction volume	$[\mathrm{L^3}]$
W	sorbent weight	[M]
x	reaction order	[–]

Subscripts

Symbol	Description
0	at the start of the reaction
e	at equilibrium
f	relative final state
i	relative initial state
j	at some state within the reaction interval under consideration
n	at the state following the last sample volume withdrawn
t	at time t