RESEARCH ARTICLE

The Pseudo-Second-Order Model in Adsorption Kinetics: Why a Good Fit Does Not Prove a Two-Site Chemisorption Mechanism

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Abstract

The pseudo-second-order (PSO) model, popularized by Ho and McKay's work on divalent metal sorption onto peat, is routinely misinterpreted as proof of a two-site chemisorption mechanism. This article provides a rigorous, multi-faceted refutation of that inference. It demonstrates that a PSO fit offers no mechanistic proof through three converging lines of evidence. First, the PSO rate law is mathematically non-unique: it emerges as a limiting case from Langmuir kinetics, intraparticle diffusion, and statistical rate theory. Most critically, the two-site Coleman mechanism itself yields a mixed-order rate equation in which pure PSO appears only under restrictive conditions; a formal reductio ad absurdum further reveals that interpreting PSO as a two-site signature contradicts its own short-time behavior. Second, the linearized fitting method suffers from spurious correlation and statistical bias. Third, the independent-site collision required by the mechanism is physically implausible for solid adsorbents. The routine practice of inferring a chemisorption pathway from a PSO fit must be replaced by independent experimental validation.

Keywords: pseudo-second-order model, adsorption kinetics, chemisorption mechanism, Langmuir kinetics, intraparticle diffusion, statistical rate theory.

1 Introduction

Few equations in adsorption science have achieved the ubiquity of the pseudo-second-order (PSO) kinetic model. Its systematic development and popularization by Ho and McKay, culminating in a comprehensive study of divalent metal ion sorption onto sphagnum moss peat [1], provided a remarkably effective method for correlating kinetic data. The origin of the second-order rate equation for adsorption is attributed to Blanchard et al. [2], who first employed such an expression for divalent metal ion exchange on zeolites. The model is expressed in its differential form as:

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$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \tag{1}$$

and in its widely used linearized expression as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_t $(\mathrm{mg\,g^{-1}})$ is the amount of solute adsorbed at time t (min), q_e $(\mathrm{mg\,g^{-1}})$ is the equilibrium sorption capacity, and k_2 $(\mathrm{g\,mg^{-1}\,min^{-1}})$ is the pseudo-second-order rate constant. Equation (2) routinely yields coefficients of determination (R^2) approaching unity. The model was derived from the explicit assumption that sorption proceeds via the Coleman two-site mechanism, as described by the reactions:

$$2\mathrm{P^-} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{CuP_2} \tag{3}$$

$$2\mathrm{HP} + \mathrm{Cu^{2+}} \rightleftharpoons \mathrm{CuP_2} + 2\mathrm{H^+} \tag{4}$$

where $\mathrm{P^-}$ and HP represent polar sites on the peat surface [3]. The rate-limiting step was presumed to be chemisorption. While the original paper presented this as a working hypothesis, it inadvertently gave rise to one of the most persistent and problematic misinterpretations in the field: that a good PSO fit constitutes direct evidence of a two-site chemisorption mechanism. It is important to emphasize that this critique does not diminish the practical utility of the PSO model as an empirical correlation for data interpolation and process design; rather, it seeks to correct the erroneous mechanistic interpretation that has become attached to it.

The first significant challenge to this mechanistic interpretation came from Azizian [4], who demonstrated mathematically that the PSO equation could be derived from the Langmuir rate law—a single-site mechanism—under conditions of low initial solute concentration, thereby severing the exclusive link between PSO kinetics and the two-site mechanism. A substantial body of subsequent theoretical work has reinforced this conclusion, showing that the PSO form can arise from a remarkably diverse range of physical scenarios, including intraparticle diffusion [5] and statistical rate theory for heterogeneous surfaces [6, 7]. In a comprehensive review, Hubbe et al. [8] subsequently consolidated these findings, concluding unequivocally that "such fits do not provide evidence of chemisorption" and that the PSO model is best regarded as a flexible empirical equation rather than a mechanistic probe. More recently, Tran [9] articulated that this misinterpretation persists widely in the literature, with many researchers explicitly labeling the PSO model as a "chemisorption" model and drawing mechanistic conclusions solely from statistical fits, often in direct contradiction to thermodynamic data such as low activation energies characteristic of physisorption. These critiques highlight a systemic methodological flaw that continues to undermine the mechanistic analysis of novel adsorbents developed for water and wastewater treatment.

This study provides a systematic, multi-faceted refutation of that mechanistic inference. It is demonstrated that a PSO fit provides no proof for any specific adsorption mechanism. The argument rests on three independent and converging pillars: the mathematical non-uniqueness of the PSO rate law, a critical statistical bias in its linearized fitting method, and the physical implausibility of its underlying mechanistic assumptions. Most decisively, it is shown that even the Coleman two-site mechanism-the very mechanism upon which the PSO model was founded-does not intrinsically yield pure PSO kinetics, and that interpreting PSO as a mechanistic signature leads to a formal logical contradiction. While the arguments presented herein are mathematical and logical in nature, their practical consequence is immediate: they liberate researchers from the unwarranted constraint of associating kinetic fits with specific molecular mechanisms, allowing engineering efforts to focus on the empirical design and optimization of adsorption processes without the distraction of unsubstantiated mechanistic claims.

2 The Non-Uniqueness of the PSO Rate Law

A fundamental principle of chemical kinetics is that a macroscopic rate law does not uniquely determine a reaction mechanism. The PSO equation is a textbook illustration: identical mathematical forms arise from profoundly different physical origins, as illustrated schematically in Figure 1.

2.1 Derivation from Langmuir Surface Reaction Kinetics

Azizian [4] first demonstrated that for a batch adsorption system, the general reversible Langmuir rate equation simplifies to the PSO form under the condition of low initial solute concentration. Marczewski [10] and Zhang [11] later derived analytical solutions, confirming that the PSO model is a special limiting case of Langmuir kinetics, approached when the dimensionless equilibrium

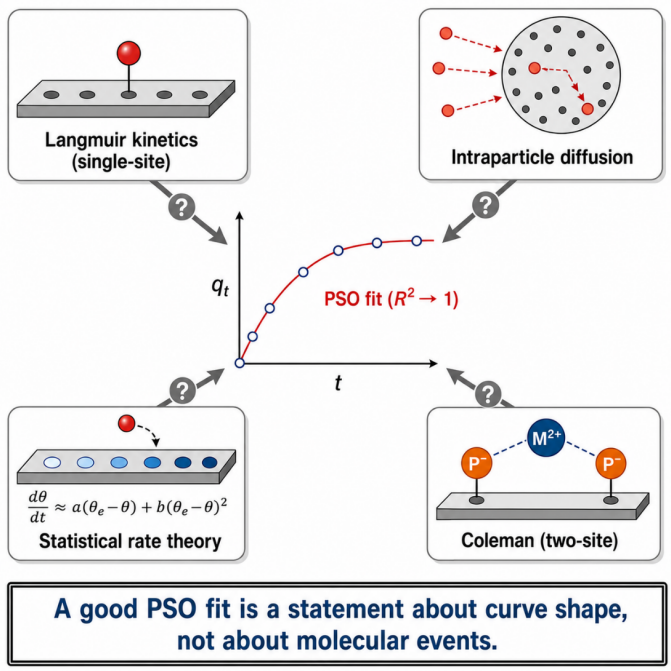

Figure 1. Schematic illustration of the non-uniqueness of the PSO model. The same PSO curve (center) can be generated by four distinct physical mechanisms: Langmuir kinetics, intraparticle diffusion, statistical rate theory, and the Coleman two-site mechanism. All four pathways lead to an indistinguishable PSO fit, highlighting its lack of mechanistic specificity.

coverage factor tends to unity. Most recently, Ezzati et al. [12] obtained the exact integrated solution of the Langmuir rate equation and demonstrated through numerical simulation that the PSO form emerges only under the twin conditions of vanishing equilibrium solution concentration ($C_e \to 0$, where C_e is the equilibrium solute concentration in solution) and surface coverage near unity ($\theta_e \to 1$, where θ_e is the equilibrium fractional coverage). These conditions are highly idealized and rarely encountered in practice. Consequently, even a system following pure, single-site Langmuir kinetics can produce data that are well-fitted by the PSO model, making the two indistinguishable by curve-fitting alone.

2.2 Derivation from Intraparticle Diffusion Control

Plazinski et al. [5] provided compelling evidence that the PSO model can accurately approximate purely diffusion-controlled kinetics. Using the intraparticle diffusion model (IDM) for spherical particles-a system entirely devoid of any chemical reaction step-they generated uptake curves that were fitted with high precision to the PSO equation. This theoretical finding is corroborated by a large body of experimental evidence. As documented by Hubbe et al. [8], numerous studies have reported excellent fits to both the PSO model and the Weber-Morris intraparticle diffusion model for the same datasets, including systems as diverse as methylene blue on wheat shells and Cu(II) on silica. Such dual fits would be impossible if the PSO model uniquely identified a two-site surface reaction mechanism. This finding shows that a good PSO fit is powerless to exclude a purely physical, diffusion-limited mechanism.

2.3 Derivation from Statistical Rate Theory and Energetic Heterogeneity

Rudzinski and Plazinski [6, 7] applied the Statistical Rate Theory (SRT) to adsorption on energetically heterogeneous surfaces, assuming a rectangular distribution of adsorption energies. For a volume-dominated system with this energy distribution, the exact SRT rate expression, when expanded in a Taylor series around equilibrium, contains only odd powers of the deviation from equilibrium (first, third, fifth, ...). A pure quadratic (PSO) term does not appear in this expansion. Nevertheless, the authors demonstrated that when the linear (pseudo-first-order) term alone is insufficient to capture the kinetics-particularly for strongly heterogeneous surfaces or systems that are not strictly volume-dominated-the empirical pseudo-second-order equation can effectively mimic the combined contribution of the first- and third-order terms. This provides a thermodynamic, rather than a steric, rationale for the empirical success of the PSO model, further severing any necessary link to a specific binding geometry.

2.4 The Critical Case: The Coleman Two-Site Mechanism and the Unifying Structural Principle

The most decisive argument comes from the very mechanism used to justify the model. Ezzati [13] recently derived the exact, general rate law for the Coleman mechanism ($\mathrm{A} + 2\mathrm{S} \rightleftharpoons \mathrm{AS}_2$), the same process invoked by Ho and McKay [1]. The exact differential equation is a linear combination of pseudo-first-order (PFO), pseudo-second-order (PSO), and pseudo-third-order (PTO) terms:

$$\frac{dq_t}{dt} = \kappa_1 (q_e - q_t) + \kappa_2 (q_e - q_t)^2 + \kappa_3 (q_e - q_t)^3 \quad (5)$$

where κ_1 (min^{-1}), κ_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$) and κ_3 ($\mathrm{g^2\,mg^{-2}\,min^{-1}}$) are lumped coefficients determined by the elementary rate constants and the operating

conditions; they are distinct from the PFO rate constant k_1 (min^{-1}) and the PSO rate constant k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$).

This analysis mathematically proves that the pure PSO form is not an intrinsic property of the two-site mechanism. Instead, it is an approximation that dominates only under a highly restrictive set of conditions: low adsorbent dosage, low specific surface area, high adsorbate molecular weight, and an equilibrium coverage fraction close to unity. Outside this narrow parametric window, the kinetics of a genuine two-site mechanism will exhibit significant first-order and third-order contributions, deviating from pure second-order behavior. The logical consequences are profound for mechanistic inference: a true two-site mechanism may not yield a good PSO fit under many experimental conditions, and a good PSO fit is a possible outcome of several entirely different physical scenarios. The PSO equation is, therefore, mathematically congruent with surface reaction (Langmuir or Coleman), diffusion control, and heterogeneous surface effects. It provides no mechanistic discrimination.

A deeper pattern emerges from the foregoing analyses. Whether one begins with the single-site Langmuir mechanism or the two-site Coleman mechanism, the exact rate equation is invariably a linear combination of multiple reaction orders. For Langmuir kinetics, the exact solution is a combination of pseudo-first-order and pseudo-second-order terms [12]. For the Coleman mechanism, the exact rate law is a combination of pseudo-first-, pseudo-second-, and pseudo-third-order terms [13]. The pure PSO form is not the fundamental equation of either mechanism; it is merely the term that dominates under a specific, narrow set of parametric conditions. This structural symmetry reveals that the PSO model is not a unique mechanistic signature but an emergent mathematical approximation that can surface from fundamentally different physical realities. Thus, no matter which mechanism one assumes, PSO is never the whole story-it is only a fragment.

2.5 A Probabilistic Reductio ad Absurdum: Why the Two-Site Interpretation Logically Fails

The mechanistic interpretation of the PSO model can be further refuted through a formal reductio ad absurdum. Assume, for the sake of argument, that the PSO rate equation is the intrinsic kinetic law of a two-site chemisorption mechanism, as originally proposed [1]. In such a mechanism, the probability of a divalent ion encountering two adjacent vacant sites is proportional to $(1-\theta)^2$, where θ is the fractional surface coverage. At the earliest moments of adsorption ($t \to 0$), the surface is nearly bare ($\theta \approx 0$), and the density of vacant site pairs is at its absolute maximum. One would therefore logically predict that the initial adsorption kinetics should be dominated by second-order behavior if this mechanism were operative.

The mathematics of the PSO model, however, yields the opposite prediction. As demonstrated by Hu et al. [14], at very short times, the integrated PSO equation reduces, via the approximation $\ln(1 + k_2 q_e t) \approx k_2 q_e t$, to the linearized pseudo-first-order (PFO) form: $\ln(q_e - q_t) = \ln q_e - k_2 q_e t$. In other words, precisely when the physical conditions for two-site adsorption are most favorable, the PSO model predicts behavior that is mathematically indistinguishable from a first-order process. This is at odds with the mechanistic interpretation.

A parallel contradiction emerges from the very practice of labeling PFO as a single-site indicator and PSO as a dual-site indicator. Both contradictions stem from the same root: the empirical pseudo-first-order and pseudo-second-order models are mathematical approximations that happen to fit kinetic data, not fundamental rate laws uniquely derived from specific molecular mechanisms. If the labeling were valid, a single-site Langmuir system should exclusively exhibit PFO behavior, and a dual-site Coleman system should exclusively exhibit PSO behavior. The mathematical reality is the reverse: the exact Langmuir rate law generates both PFO and PSO terms [12], and the exact Coleman rate law generates PFO, PSO, and PTO terms simultaneously [13]. The appearance of a PSO term in a kinetic fit cannot, therefore, logically favor a dual-site interpretation when a single-site mechanism also produces it. The practice of assigning mechanistic meaning to these empirical models is thus logically inconsistent. Both mixed-order structures are summarized in Figure 2.

The contradiction can only be resolved by rejecting the initial assumption: the PSO equation is not the fundamental rate law of a two-site mechanism. Nor, it must be stressed, can one salvage the argument by claiming that the PFO form observed at short times implies a single-site mechanism. As established in Section 2.1, pure PFO behavior is merely another idealized limit of the Langmuir rate law [12]. Thus, neither PSO nor PFO is a unique mechanistic signature. Both are flexible mathematical approximations that

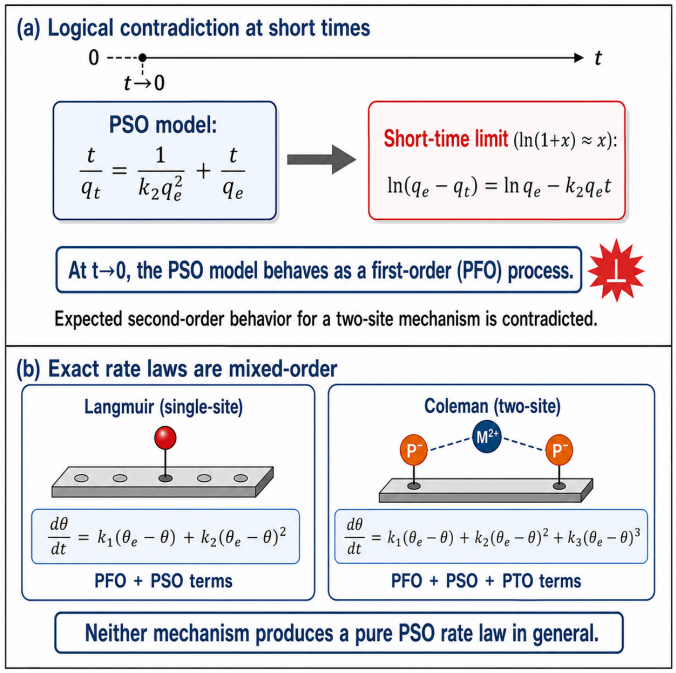

Figure 2. Schematic of the reductio ad absurdum. (a) At short times, the integrated PSO equation reduces to a linear pseudo-first-order form, contradicting the expected second-order behavior from a two-site mechanism. (b) The mixed-order nature of exact rate laws: both Langmuir and Coleman mechanisms yield combinations of PFO, PSO, and PTO terms, showing that neither model is a unique mechanistic signature.

can emerge from multiple physical realities, and their appearance at different stages of a single kinetic curve provides no discriminatory power whatsoever.

A concise overview of the key derivations discussed in this section is provided in Table 1, allowing the reader to trace the logical steps from fundamental rate laws to their PSO-limiting forms.

3 Methodological Bias: Spurious Correlation in the Linearized Plot

The reported superiority of the PSO model over the pseudo-first-order (PFO) model in Ho and McKay [1] was established using the extremely high correlation coefficients (R^2) of the linearized t/q_t versus t plot. This methodology is now recognized as fundamentally flawed and statistically biased.

Simonin [15] demonstrated that including data points close to equilibrium in the linearized analysis distorts the error structure, creating a systematic bias that unfairly favors the PSO model. He concluded that the widely reported dominance of PSO over PFO is largely a methodological artifact. Xiao et al. [16] provided a rigorous mathematical proof of spurious correlation: as $t \to \infty$, the term t/q_e in the linearized equation becomes dominant, forcing R^2 toward unity irrespective of the true underlying kinetic model, even for data generated from a random process. Bujdák [17] empirically confirmed this by generating ideal PFO kinetic data and fitting it with the linear PSO model, obtaining a near-perfect $R^2 > 0.99$. This demonstrates conclusively that the metric is non-diagnostic. Therefore, a high R^2 from the linearized PSO plot cannot distinguish between first- and second-order kinetics and is a completely invalid metric for mechanistic diagnosis.

To illustrate the severity of this statistical artifact, we conducted a numerical simulation in which synthetic adsorption data were generated from a true pseudo-first-order (PFO) process and subsequently fitted to the linearized PSO equation. The simulation parameters and the resulting PSO regression output are summarized in Table 2, and the corresponding plot demonstrating the spurious correlation is presented in Figure 3. Despite the data originating from a purely first-order mechanism, the linearized PSO plot yields an R^2 value approaching unity ($R^2 = 0.9954$) and produces seemingly reasonable PSO parameters ($q_e \approx 114.3\ \mathrm{mg\,g^{-1}}$, $k_2 \approx 1.18 \times 10^{-3}\ \mathrm{g\,mg^{-1}\,min^{-1}}$). This outcome underscores a critical point: a high R^2 from a linearized PSO plot is not a reliable indicator of the underlying kinetic mechanism and cannot distinguish between first-order and second-order processes. Indeed, when the fitted PSO curve is back-transformed to the q_t domain, the root mean square error (RMSE) is $3.02\ \mathrm{mg\,g^{-1}}$, six times the imposed noise level, exposing the misfit that the high R^2 conceals. In addition, the RMSE provides a more reliable assessment of model fit because it directly quantifies the average deviation between experimental and calculated values, unlike R^2, which can be artificially inflated [18].

4 Physical Implausibility of Independent Surface Sites

For the PSO equation to represent an elementary rate law via the law of mass action for the reaction $2\mathrm{P}^- + \mathrm{M}^{2+} \rightleftharpoons \mathrm{MP}_2$, the rate must be proportional to the square of the concentration of vacant sites. This statistical requirement implicitly demands that pairs of vacant, polar sites (P^-) behave as independent, mobile entities capable of random collision and reorientation. As thoroughly critiqued by Hubbe et al. [8], this picture is physically unrealizable for functional groups anchored to a solid, cross-linked adsorbent matrix.

Table 1. Summary of key mathematical derivations demonstrating the emergence of the pseudo-second-order form from distinct physical mechanisms.

Equation / Concept	Starting Point	Key Assumptions	Key Steps	Ref.
Derivation of PSO from Langmuir kinetics	$\frac{d\theta}{dt} = k_a(C_0-\beta\theta)(1-\theta)-k_d\theta$	Batch system; mass balance $C = C_0 - \beta\theta$; low initial solute concentration C_0; very short initial adsorption times ($t \to 0$).	The general solution for $\theta(t)$ is obtained by integrating the full rate equation without neglecting any terms. For $\lambda t \ll 1$ (short times), the approximation $e^{\lambda t} \approx 1 + \lambda t$ is applied to this solution, which after rearrangement yields the linearized pseudo-second-order equation.	[4]
Exact integrated Langmuir (EIL) rate law	$\frac{d\theta}{dt} = k_a(C_0-\beta\theta)(1-\theta)-k_d\theta$	Langmuir adsorption mechanism; mass balance $C = C_0 - \beta\theta$; equilibrium constant $K = \frac{\theta_e}{(C_0 - \beta\theta_e)(1-\theta_e)}$	The rate equation is algebraically rearranged into a mixed PFO-PSO form: $\frac{d\theta}{dt} = k_a\frac{C_0 - \beta\theta_e^2}{\theta_e}(\theta_e-\theta)+k_a\beta(\theta_e-\theta)^2$. The PSO model emerges if and only if $C_0 \approx \beta\theta_e^2$ (i.e., the PFO term vanishes).	[12]
Statistical Rate Theory (SRT)	$\frac{d\theta_t}{dt} = K_{ls}c^{(e)}\left(1-\theta_t^{(e)}\right)\times \left[\exp\left(\frac{\mu_b-\mu_s}{kT}\right) - \exp\left(\frac{\mu_s-\mu_b}{kT}\right)\right]$	Langmuir adsorption model; strongly heterogeneous solid surface characterized by a rectangular adsorption energy distribution $\chi(\varepsilon) = \text{const}$; volume-dominated system ($c \approx c^{(e)}$); quasi-equilibrium on the solid surface.	Express chemical potentials μ_b and μ_s using the Langmuir model and the condensation approximation for the heterogeneous surface; substitute into the SRT rate expression; expand the resulting exponential difference in a Taylor series around $\theta_t = \theta_t^{(e)}$; retain the leading linear term. The PSO model is not a strict mathematical limit of the SRT; it can, however, serve as an effective empirical approximation when the linear term alone is insufficient, because it mimics the combined effect of the first- and third-order contributions.	[6, 7]
Coleman mechanism exact rate law	$\frac{d\theta}{dt} = k_a(C_0-\beta\theta)(1-\theta)^2 - k_d\theta$	Coleman two-site mechanism ($A + 2S \rightleftharpoons AS_2$); mass balance $C = C_0 - \frac{m_a}{V}\frac{A_S}{2La_S}\theta$, where m_a is the adsorbent mass, V the solution volume, A_S the specific surface area, a_S the contact surface area of an adsorbed particle, and L the Avogadro constant.	Insert the mass balance into the rate equation. Replace k_d/k_a using the equilibrium constant derived from the Coleman mechanism. Rearrange to collect terms of like order in $(\theta_e - \theta)$, yielding an expression proportional to $(\theta_e - \theta)$, $(\theta_e - \theta)^2$ and $(\theta_e - \theta)^3$. The pure PSO form is recovered if and only if $\frac{m_a}{V}\frac{A_S}{2La_S} \to 0$ and $\theta_e \to 1$ (i.e., low adsorbent dosage, low specific surface area, high adsorbate molecular weight, and near-unity equilibrium coverage).	[13]

Notation: θ, fractional surface coverage (θ_e at equilibrium); C, C_0, solute concentration at time t and initially; k_a, k_d, adsorption and desorption rate constants; $K = k_a/k_d$, equilibrium constant; β, proportionality factor linking coverage to solution depletion in the mass balance (for Langmuir, $\beta = m_a q_m/V$ with q_m the monolayer capacity in molar units); λ, characteristic rate parameter of the integrated Langmuir solution; K_{ls}, SRT rate constant; $c^{(e)}$, equilibrium bulk concentration; μ_b, μ_s, chemical potentials of the solute in the bulk and adsorbed phases; k, Boltzmann constant; T, absolute temperature.

Although bidentate or multidentate coordination is well documented in surface chemistry, the macroscopic rate law describing the overall uptake need not reflect the stoichiometry of the final binding state. Even when a divalent cation ultimately coordinates with two adjacent functional groups, these groups form a single, static bidentate binding site. Consequently, the molecularity of the elementary binding step relative to the surface sites is unlikely to be two, and thus the quadratic dependence on $(q_e - q_t)$ cannot serve as evidence for a dual-site elementary reaction.

Furthermore, adsorption processes are frequently

Table 2. Input parameters and output results of the numerical simulation demonstrating spurious correlation in the linearized pseudo-second-order plot. Synthetic data were generated from a true pseudo-first-order process and fitted to the linearized PSO equation.

Parameter	Value
True q_e ($\mathrm{mg\,g^{-1}}$)	100.00
True k_1 ($\mathrm{min^{-1}}$)	0.100
Time range (min)	0-60
Number of points (evenly spaced; $t = 0$ excluded from fit)	20 (19 fitted)
Noise standard deviation ($\mathrm{mg\,g^{-1}}$)	0.50
Random seed	42
PSO fit R^2	0.9954
Estimated q_e ($\mathrm{mg\,g^{-1}}$)	114.31
Estimated k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	1.180×10^{-3}
RMSE of back-calculated q_t ($\mathrm{mg\,g^{-1}}$)	3.02

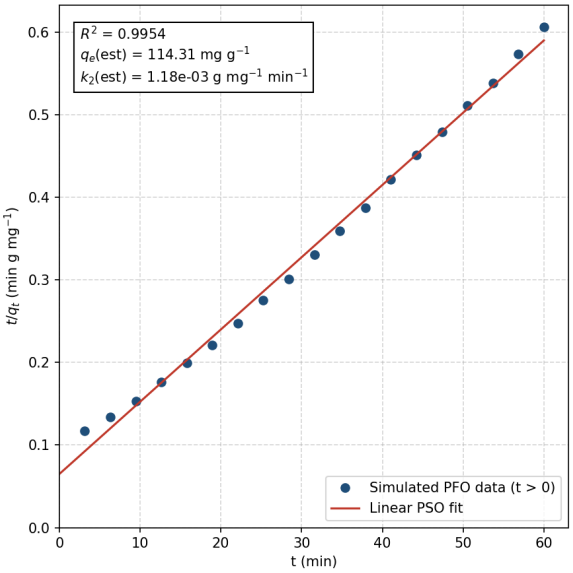

Figure 3. Statistical bias in the linearized pseudo-second-order (PSO) plot. Synthetic data were generated from a true pseudo-first-order (PFO) process ($q_e = 100\ \mathrm{mg\,g^{-1}}$, $k_1 = 0.1\ \mathrm{min^{-1}}$) with added Gaussian noise (standard deviation $0.5\ \mathrm{mg\,g^{-1}}$) and subsequently fitted to the linearized PSO equation, Eq. (2). The fit yields an R^2 value of 0.9954 despite the data originating from a PFO mechanism, illustrating the spurious correlation inherent in the linearized plot and its inability to discriminate between kinetic models. The complete Python script used to generate this figure is provided in the Supplementary Material.

accompanied by pH shifts that alter both the speciation of the solute and the surface charge of the adsorbent [19]. Such dynamic changes can cause the equilibrium capacity q_e to vary during the experiment, yet the PSO model treats q_e as a time-invariant constant. This additional discrepancy further undermines any mechanistic inference drawn solely from the fitted curve shape.

5 Conclusions

The PSO model is a valuable empirical correlation tool, but its excellent data-fitting capability does not constitute evidence for a two-site chemisorption mechanism. The converging mathematical, statistical, and physical arguments presented here demonstrate that a PSO fit is mechanistically non-diagnostic. In particular, the Coleman two-site mechanism does not yield pure PSO kinetics, and interpreting PSO as a two-site signature is at odds with its own short-time behavior. The situation exemplifies the principle of underdetermination: when identical kinetic data can be equally well described by several mutually exclusive physical frameworks, the data alone cannot single out one mechanism over the others. A good PSO fit merely reflects the shape of the uptake curve, not the molecular events that generated it.

From a practical standpoint, incorrectly labeling a process as chemisorption can misguide decisions on adsorbent regeneration and reuse. If strong chemical bonding is assumed, engineers may select aggressive or costly regeneration methods unnecessarily, or, conversely, may abandon attempts at regeneration under the belief that the adsorbate is irreversibly bound. Accurate mechanistic understanding, based on independent spectroscopic and calorimetric evidence rather than curve fitting, is therefore essential for assessing the long-term feasibility, operational costs, and sustainability of adsorption technologies.

The routine practice of inferring a chemisorption pathway from a PSO fit must be discontinued. True mechanism elucidation requires independent experimental evidence. For the practicing engineer, the PSO model remains a convenient empirical correlation for data interpolation and process design, but mechanistic conclusions should be reserved for systems with independent spectroscopic or computational support. In the absence of such evidence, model selection for design purposes should be guided by information-theoretic criteria, such as the Akaike or Bayesian information criterion (AIC/BIC), applied to nonlinear fits rather than by mechanistic assumptions. Only by separating phenomenological modeling from mechanistic interpretation can the field advance with scientific rigor.

Data Availability Statement

Data will be made available on request.

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Conflicts of Interest

Maryam Azizi is affiliated with the Persian Iran Gas Company, Tehran, Iran. The authors declare that this affiliation had no influence on the study design, data collection, analysis, interpretation, or the decision to publish, and that no other competing interests exist.

AI Use Statement

The authors declare that DeepSeek was used for language and grammar editing of the manuscript. The authors have carefully reviewed, revised, and verified the AI-assisted output and take full responsibility for the content of the manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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Supplementary Material

S1. Overview

This supplementary section contains the complete Python script used to generate the synthetic kinetic data, perform the linearized PSO regression, and produce Figure 3 and Table 2. The script requires Python 3.11 with NumPy, SciPy, and Matplotlib. No additional dependencies are needed.

S2. Python Script

```
import numpy as np
import matplotlib.pyplot as plt
from scipy import stats

# ==================== INPUT PARAMETERS ====================
qe_true     = 100.0   # true equilibrium capacity (mg/g)
k1_true     = 0.1     # true PFO rate constant (1/min)
t_max       = 60.0    # total time (min)
n_points    = 20      # number of data points
noise_level = 0.5     # std of Gaussian noise (mg/g)
random_seed = 42      # for reproducibility

np.random.seed(random_seed)

# ==================== GENERATE TRUE PFO DATA ====================
t       = np.linspace(0, t_max, n_points)
q_true  = qe_true * (1 - np.exp(-k1_true * t))
q_noisy = q_true + np.random.normal(0, noise_level, size=n_points)

# ==================== LINEARIZED PSO FIT ====================
# Exclude t = 0 to avoid division by zero (19 points fitted)
t_fit    = t[1:]
q_fit    = q_noisy[1:]
t_over_q = t_fit / q_fit

slope, intercept, r_value, p_value, std_err = \
    stats.linregress(t_fit, t_over_q)
r_squared = r_value ** 2

# ==================== EXTRACT PSO PARAMETERS ====================
qe_est = 1.0 / slope
k2_est = 1.0 / (intercept * qe_est**2)

# ==================== RMSE IN q_t DOMAIN ====================
q_pso_back = qe_est * (1 - 1 / (1 + k2_est * qe_est * t_fit))
rmse = np.sqrt(np.mean((q_fit - q_pso_back)**2))

# ==================== OUTPUT ====================
print(f"PSO fit R^2                  {r_squared:.4f}")
print(f"Estimated qe (mg/g)          {qe_est:.2f}")
print(f"Estimated k2 (g/(mg*min))    {k2_est:.6f}")
print(f"RMSE (mg/g)                  {rmse:.4f}")
```

```
# ==================== PLOTTING ====================
plt.rcParams.update({'font.family': 'Arial', 'font.size': 12})
fig, ax = plt.subplots(figsize=(6, 6))

t_line       = np.linspace(0, t_max, 200)
t_over_q_fit = intercept + slope * t_line

ax.plot(t_fit, t_fit / q_fit, 'o',
        color='#1A5276', markersize=8, label='Simulated PFO data')
ax.plot(t_line, t_over_q_fit, '-',
        color='#C0392B', linewidth=2, label='Linear PSO fit')

textstr = (f'$R^2 = {r_squared:.4f}$\n'
           f'$q_e$(est) = {qe_est:.2f} mg/g\n'
           f'$k_2$(est) = {k2_est:.4f} g/(mg$\cdot$min)')
ax.text(0.05, 0.95, textstr, transform=ax.transAxes, fontsize=11,
        verticalalignment='top', color='black',
        bbox=dict(boxstyle='square,pad=0.5', facecolor='white',
                  edgecolor='black', linewidth=1))

legend = ax.legend(loc='lower right', frameon=True,
                   edgecolor='black', facecolor='white',
                   fontsize=11, fancybox=False)
legend.get_frame().set_linewidth(1)

ax.set_xlabel('t (min)', fontsize=14)
ax.set_ylabel('t/q_t (min g/mg)', fontsize=14)
ax.tick_params(axis='both', colors='black')
ax.grid(True, linestyle='--', alpha=0.4, color='#7F8C8D')
ax.set_xlim(left=0)
ax.set_ylim(bottom=0)
for spine in ax.spines.values():
    spine.set_edgecolor('black')
    spine.set_linewidth(1)

plt.tight_layout()
plt.savefig('Figure3.png', dpi=300, bbox_inches='tight')
plt.show()
```

S3. Expected Console Output

```
PSO fit R^2                 0.9954
Estimated qe (mg/g)         114.31
Estimated k2 (g/(mg*min))   0.001180
RMSE (mg/g)                 3.0180
```

Note: Minor differences of ± 1 in the last decimal place may arise from OS or library version differences and do not affect any conclusion of the study.

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