A revised pseudo-second order kinetic model for adsorption, sensitive to changes in adsorbate and adsorbent concentrations

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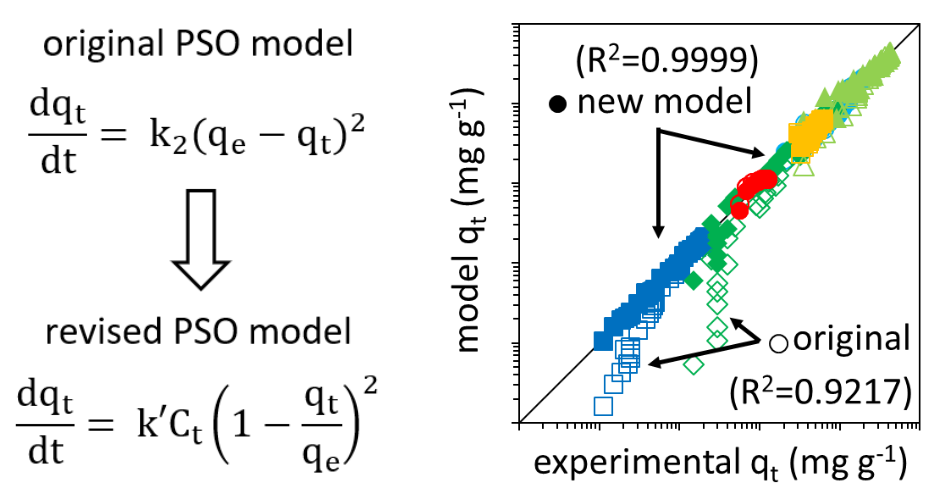
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# Graphical Abstract



# Keywords

Adsorption kinetics; kinetic model; pseudo-second order; Lagergren; water treatment; particle size

# Abstract

The development of new adsorbent materials for the removal of toxic contaminants from drinking water is crucial towards achieving the United Nations Sustainable Development Goal 6 (clean water and sanitation). The characterisation of these materials includes fitting models of adsorption kinetics to experimental data, most commonly the pseudo-second order (PSO) model. The PSO model, however, provides no sensitivity to changes in experimental conditions such as adsorbate and adsorbent concentrations (C0 and Cs) and consequently is not able to predict changes in performance as a function of operating conditions. Furthermore, the experimental conditionality of the PSO rate constant, k2, can lead to erroneous conclusions when comparing literature results. In this study, we analyse 103 kinetic experiments from 47 literature sources to develop a relatively simple modification of the PSO rate equation, yielding:

Unlike the original PSO model, this revised rate equation (rPSO) provides the first-order and zero-order dependencies upon C0 and Cs that we observe empirically. Our new model reduces the residual sum of squares by 66% when using a single rate constant to model multiple adsorption experiments with varying initial conditions. Furthermore, we highlight how the rPSO rate constant k’ is more appropriate for literature comparison, highlighting faster kinetics in the adsorption of arsenic onto alumina versus iron oxides. This revised rate equation should find applications in engineering studies, especially since the rPSO rate constant k’ does not show a counter-intuitive inverse relationship with increasing reaction rates when C0 is increased, unlike the PSO rate constant k2.

# Introduction

There is a wealth of recent literature concerning the development of novel adsorbent materials for the remediation of contaminated water, such as composite materials offering superior stability 1, ease of separation from the effluent 2 3, or multifunctional capabilities such as photocatalytic activity 4 5. Energy input typically forms about one third of water treatment plant operation costs 6, and if energy efficiencies are to be improved then accurate models of adsorption kinetics (including rate constants) are needed to (a) identify the minimum mixing time necessary for batch treatments and (b) estimate maximum flow rates for column or continuous-flow treatments 7. Laboratory experiments can only partially capture the environments in which new adsorbents will operate, and in practice different concentrations of adsorbent (Cs) will be needed to treat different concentrations of contaminant in the influent (C0). It is thus important that adsorption models are made sensitive to operating conditions, providing predictive capabilities.

Currently, the pseudo-second order (PSO) rate equation 8, popularised by Ho and McKay (1999) 9, is probably the most widely used model for adsorption kinetics 10. The PSO rate equation takes the form:

Equation 1

where t is time (minutes), qt is the amount of adsorbate adsorbed per mass of adsorbent at time t (mg g-1), k2 is the pseudo-second order rate constant (g mg-1 min-1), and qe is the amount of adsorbate adsorbed at equilibrium (mg g-1) 9.

The decrease in the concentration of aqueous adsorbate with time is given by the equation:

Equation 2

where Ct is the concentration of aqueous adsorbate at time t (mg L-1), C0 is the initial adsorbate concentration at t=0 (mg L-1) and Cs is the concentration of adsorbent (g L-1).

The PSO model is popular for several reasons. Firstly, it has a simple mathematical form. Secondly, whilst the PSO rate equation was originally rationalised as a mechanistic model for describing the bidentate adsorption of copper onto peat 11, the PSO model is able to fit kinetic data for a wide range of systems with different reaction mechanisms 9 12 13 (including where diffusion control is to be expected 14). Thirdly, Equation 1 can be integrated and rearranged to provide linear equations (of the form y=mx+c) from which the model parameters k2 and qe can be easily obtained by linear regression 15.

However, the PSO model has several important limitations due to the concentrations of adsorbate and adsorbent not being included within the rate equation, with k2 and qe parameters only being valid for the experimental conditions under which the PSO model was fitted. The first limitation is that the model cannot predict how adsorption kinetics will change as a function of C0 and Cs, limiting the usefulness of the PSO model, especially in engineering or optimisation studies. Furthermore, rate constants from different literature sources with different experimental conditions cannot be meaningfully compared: greater values of k2 do not necessarily indicate adsorbents with superior adsorption kinetics.

The aim of the present study was to modify the popular PSO equation, introducing sensitivity towards changes in C0 and Cs, with the objective of both improving predictive capabilities for engineering studies and normalising rate constants for meaningful comparison between literature sources. Given its ability to describe a wide range of systems, the PSO model does not necessarily reveal insights into the adsorption mechanisms (i.e. whether intraparticle diffusion or chemisorption is the rate determining step) 13 16, and our aim was similarly to develop an empirical model, rather than a mechanistic model. We thus conducted an empirical analysis of the adsorption kinetics reported by the literature to assess the influence of C0 and Cs on adsorption rates, and to modify the PSO rate equation accordingly.

We used the method of initial rates to determine the order of reaction with respect to both C0 and Cs (given the possibility for data at later times to disguise the true reaction order 17, such as when slower surface precipitation processes coincide with monolayer adsorption 18). We first performed quality control experiments, investigating different methods for calculating initial rates when the availability of early kinetic data is limited (as per many adsorption experiments). We then compiled a wide range of literature data sets wherein multiple adsorption kinetic experiments with different values of C0 and Cs are reported (with each data set being a specific adsorbate-adsorbent system) and determined the order of reaction with respect to each variable. We used mineral and organic adsorbents, and metal, inorganic and organic adsorbates, to achieve a model that is generally applicable to a wide range of systems, as per the original PSO model. We built the observed C0 and Cs dependence into a revised form of the PSO rate equation (which we refer to as the rPSO rate equation) and verified that the rate constants given by this new model are more stable with respect to changes in experimental conditions than the PSO rate constant k2. Finally, we used two application studies to assess the potential of this revised PSO model to overcome current limitations: (1) describing multiple experiments with varying values of C0 and Cs using a single rate constant, and (2) achieving a more meaningful comparison of the adsorption kinetics reported across the literature.

# Experimental

## Data sets

Literature sources that experimentally investigated the influence of C0 and Cs upon adsorption kinetics were compiled and the experimental data was tabulated (as referenced in the Supplementary Information: SI Table S1). Both mineral adsorbents and organic adsorbents (activated carbon and chitosan) were included, however zeolites and metal-organic frameworks (MOFs) were not since the sorption mechanism of adsorbate trapping within cages might produce contrary results. None of the literature sources found gave any mechanistic account or mathematical explanation for observed differences in adsorption kinetics due to varying values of C0 or Cs. The majority of the compiled literature used the PSO model to describe adsorption kinetics.

In total 47 literature sources with approximately 100 kinetic experiments were collected. This includes: 14 literature sources reporting early kinetic data (where ) to investigate how the availability of early kinetic data influences initial rate calculations; 8 literature sources (9 data sets) with a total 37 experiments where C0 is varied; 6 literature sources (8 data sets) with a total 27 experiments where Cs is varied; and 21 literature sources (25 experiments) for the adsorption of inorganic arsenic onto iron oxide and alumina adsorbents. A data set is considered to be all kinetic experiments using the same adsorbate-adsorbent system within a single literature source. The compiled data sets are presented elsewhere 19.

## Mathematical approaches for the determination of initial rates

Three approaches towards the calculation of initial rates were compared: (1) the initial slope, (2) linearised PSO kinetics, and (3) non-linear PSO kinetics.

Under the initial slope approach, the initial rate ( at t=0) was calculated as the slope between the origin at (0,0) and the earliest available data point at t>0 20.

Initial rates were also calculated using the following linearised form of the integrated PSO rate equation:

Equation 3

Kinetic profiles were plotted as as a function of t and the linear regression was obtained using the LINEST function in Microsoft Excel (where the residual sum of squares between the data points and the linear regression is minimised). The equilibrium adsorption parameter qe was obtained via the relationship where m is the slope of the linear regression, and k2 via where c is the y-intercept. The initial rate of adsorption was then calculated through the simplification of Equation 1:

Initial rate =

Equation 4

Uncertainties in k2, qe and the initial rate were calculated by linear propagation of the standard errors in m and c given by the LINEST function.

Finally, initial rates were calculated using non-linear PSO kinetics. Non-linear fitting of the PSO model to experimental data was achieved by using Microsoft Excel’s Solver function to optimise k2 and qe values, minimising the sum of squared residuals between the model and experiment. Uncertainties in k2 and qe were calculated using a Monte-Carlo approach with 200 simulations as described by Hu et al. 21.

For all literature sources, parameters were converted to the same units for ease of comparison: k2 (g mg-1 min-1); qe (mg g-1); and the initial rate (mg g-1 min-1).

The influence of the availability of early kinetic data on the accuracy and precision of initial rates calculated using these three approaches was evaluated as follows. Fourteen data sets containing early kinetic data were collected (defined as adsorption experiments containing data within the range ). Initial rates were then re-calculated as data points were consecutively removed from the earliest to the latest. A linear regression between the calculated initial rates and the value of at the first available kinetic data point was determined and extrapolated to to provide a theoretical ‘true’ initial rate (representing the case if kinetic data were to be collected within an infinitesimally small time period). This theoretical ‘true’ initial rate was used as a reference value to determine variation in the calculated initial rate as a function of the availability of early kinetic data. A systematic error was calculated using the average error across all data sets and a random error was calculated as the standard deviation in the error across all data sets. The paired samples t-test was used to evaluate the significance of the differences observed between the errors given by each of the three mathematical approaches used for calculating initial rates.

After evaluating the three approaches (see Results and Discussion), non-linear PSO kinetics were used to determine initial rates in all subsequent calculations.

## Determining the order of reaction

The order of reaction with respect to the independent variables C0 and Cs was calculated as the slope of log(initial rate) versus log(independent variable) 22. The order of reaction was calculated for each data set (kinetic experiments using the same adsorbate-adsorbent system within a single literature source), with each data point used within the linear regression representing a single kinetic experiment at a unique value of C0 or Cs. This is represented by the equation:

Equation 5

For each data set, the order of reaction with respect to the independent variable was calculated using the LINEST function in Microsoft Excel. The uncertainty in the order of reaction for each data set was specified as the standard error of the slope. An average (mean, x̄) order of reaction representing all data sets was calculated, with errors reported as the standard deviation. The dependencies of k2 and k’ upon C0 and Cs were determined using the same method, only substituting the initial rate with k2 or k’.

## Modelling the revised rate equation

Our final rate equation, developed and derived in the Results and Discussion (Equation 9, referred to as the rPSO), is:

Equation 6

where the rate constant k’ takes the units L g-1 min-1. As the rPSO rate equation is not easily integrated, experiments were simulated using Microsoft Excel. The quantity of adsorbate adsorbed at the nth data point was calculated using the following formula:

Equation 7

The time interval between data points, or Δt, was reduced until the magnitude of Δt had no significant effect on the results. The rPSO parameters k’ and qe were obtained by non-linear fitting, using Microsoft Excel’s Solver function to minimise the sum of squared residuals between the model and experiment.

## Application studies

In the first application study, i.e. evaluating the potential of the rPSO model for predictive applications, 6 data sets were used: 3 where C0 was varied and 3 where Cs was varied. In the first step, values of the equilibrium adsorption capacity (qe) were obtained by fitting kinetic experiments individually using the PSO and rPSO models (optimising the rate constant and qe simultaneously to minimise the sum of squared residuals). In the second step, the PSO and rPSO models were fit to all experiments within the given data set simultaneously, i.e. experiments with the same adsorbate-adsorbent system but different C0 or Cs values. In this step, a unique value of qe was used for each experiment but a single value of the rate constant (k2 or k’, depending upon the model) was shared between all experiments within the data set. Here, qe was fixed to the values previously calculated and only the rate constant was optimised.

In the second application study, i.e. evaluating the potential of the rPSO rate constant k’ for more meaningful comparisons across the literature, 18 experiments reporting the adsorption kinetics of inorganic arsenic onto iron oxide minerals were collated. Both As(V) and As(III) experiments were included, since no significant difference between the adsorption kinetics was observed. A further 7 experiments reporting the adsorption of inorganic arsenic onto alumina (Al2O3) were collected for comparison. The particle radius (r) was taken as reported by each study.

# Results and Discussion

## Determination of the influence of experimental conditions (C0 and Cs) on the initial rate of adsorption

### Quality control: The calculation of initial rates and setting criteria for the selection of literature data sets

Many adsorption experiments reported by the literature begin their collection of kinetic data at high values of , where a significant proportion of the reaction has already been completed. This may be due to challenges in collecting samples quickly (especially when filtering is required), given that many adsorption reactions reach equilibrium in the minutes timescale. Other possible reasons include a lack of appreciation over the time-scale at which adsorption kinetics are best measured, with many papers fitting kinetic models to data where the reaction has already plateaued and reached equilibrium.

Whilst we chose to investigate the influence of C0 and Cs using the method of initial rates, the lack of literature reporting early stage kinetic data, i.e. low values of , is a challenge. A popular approach to calculate initial rates is to determine the slope of a line that is tangent to the experimental data curve and passes through the origin at (0,0) 20. However, the later the first kinetic data is collected, the shallower the slope will be, therefore creating a systematic underestimation of the initial rate. Application of a kinetic adsorption model allows for the extrapolation of adsorption rates to t=0, however the accuracy of the calculated initial rates depends upon how closely the experimental data follows the chosen model.

We therefore conducted a preliminary experiment to investigate how a limited availability of early kinetic data would influence the accuracy and precision of initial rates calculated using the initial slope or using the original PSO model (given that the PSO model is known to approximately describe a wide range of adsorbate-adsorbent systems 12). These results were used to set quality control criteria for which data sets would be included when investigating the influence of C0 and Cs on adsorption kinetics.

The literature search identified fourteen data sets satisfying the criteria that , a relatively small number, highlighting how most studies fail to collect early kinetic data (SI Figure S1). Initial rates calculated from the slope between the origin and the earliest available data point show the typical systematic underestimation of initial rates when early kinetic data is missing (Figure 1a, with the solid line representing the average of all data sets). In contrast, when calculated using the PSO model, there is no systematic error in the calculation of initial rates when the first kinetic data is collected within the range (Figure 1b,c). In all three approaches, significant variation between data sets is observed, i.e. an error in the initial rate unique to each data set. This error (dashed lines representing one standard deviation) is approximately constant in the initial slope approach, being significant even when early kinetic data is available. In contrast, this error is insignificant when using early kinetic data and either of the PSO approaches, though this error increases in magnitude as early data is sequentially removed.

Additionally, the absolute values of the initial rates calculated using the earliest possible kinetic data were compared, i.e. 14 initial rate calculations, with Student’s t-test indicating that both linearised PSO kinetics and non-linear PSO kinetics tend to return an initial rate greater than that calculated using the initial slope (with p=0.87 and 0.97 respectively). The increase in initial rates calculated using non-linear PSO kinetics versus linearised PSO kinetics is not significant (p=0.33 using the 14 initial rate calculations). However, when comparing the calculated initial rates with all possible data cut-offs, i.e. 115 initial rate calculations (Figure 1d), the differences are more significant: non-linear PSO kinetics return greater initial rates than linearised PSO kinetics (p=1.00). This is due to the biased weighting of linearised PSO kinetics towards data at later times, with the slope of versus t increasing as equilibrium adsorption is approached, returning smaller values of qe and thus giving a smaller initial rate. The difference between initial rates calculated using linearised and non-linear PSO kinetics was observed despite equilibrium adsorption kinetic data from the original literature being excluded in our calculations.

Finally, we considered the uncertainties in the initial rates calculated using the two PSO approaches with varying availability of early kinetic data (Figure 1e). The uncertainties in the initial rates calculated using linearised PSO kinetics were calculated from the standard error in the linear regression fit to versus t, whilst the uncertainties in non-linear PSO kinetics were calculated using synthetic data and 200 Monte-Carlo simulations 21. Using linearised PSO kinetics, the propagated uncertainty in the calculated initial rate increases exponentially as early kinetic data is removed. This is explained by how late stage adsorption data is weighted too heavily when fitting linearised PSO kinetics 10. At late stages, differences between the qt values of consecutive data points are small relative to the measurement uncertainty, increasing the uncertainty of the linear regression. At , the average uncertainty in the initial rates calculated using linearised PSO kinetics is 9.5%. In contrast, the uncertainty in the initial rates calculated using non-linear PSO kinetics is essentially independent of the availability of early kinetic data, and at the average uncertainty is only 5.7%.

As highlighted here, ideally the data sets used to explore the influence of experimental parameters such as the adsorbate concentration (C0) and the adsorbent concentration (Cs) should include early kinetic data to reduce the uncertainty in the calculated initial rates. To provide a balance between the accuracy of our initial rate calculations and the collection of a sufficient quantity of data sets for statistical analysis, we set the criterion that data sets must include kinetic data with . This boundary condition gives an average error in the calculated initial rate of -44 ±22 % for the initial slope approach, +17 ±38 % using linearised PSO kinetics, and only +3 ±27% for the non-linear PSO kinetics. The results indicate that non-linear PSO kinetics are most appropriate for calculating initial rates, with an insignificant systematic error. A ~30% uncertainty remains, associated with how closely the adsorption kinetics follow the shape of the PSO model (with deviations being both due to inaccurate measurements and real chemical mechanisms).

By considering a literature source reporting two kinetic experiments only, with a different value of C0 or Cs in each, a 30% error in the initial rate of the first experiment (as per the boundary condition of ) will confer an error of <0.5 in the calculated reaction order.

In the present study, the average value of in the first available kinetic data is 0.37 for experiments where C0 is varied, and 0.27 for experiments were Cs is varied, indicating that the uncertainties in the calculated initial rates will be <30%. Furthermore, the number of kinetic experiments in each literature data set was between 3 and 6. Under these conditions, the calculated orders of reaction will be accurate to the nearest integer value. This was deemed appropriate for the purposes of developing the revised PSO model, given that it is common practice for kinetic adsorption models to use integer values for reaction orders, e.g. the original PSO equation and the pseudo-first order kinetic model 9. In principle however, however a similar analysis could be made using non-integer orders of reaction.

Consequently, non-linear fitting of the PSO model was used to determine the initial rate of adsorption in each kinetic experiment in all subsequent work.

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| --- | --- | --- | --- |
| (a) | (b) | | (c) |
| (d) | | (e) | |

Figure 1: The influence of the limited availability of early kinetic data on the calculation of initial rates of adsorption, assessed by the analysis of 14 literature sources. The influence of removing early kinetic data on the calculated initial rates was assessed using (a) the initial slope, (b) linearised PSO kinetics, and (c) non-linear PSO kinetics. The theoretical ‘true’ initial rate is given by initial rate0 and the initial rate calculated with the available data is given by initial ratei. The solid black line represents the average of the 14 data sets, whilst dotted lines indicate one standard deviation. The three approaches are compared, assessing the influence of data availability on (d) the relative error in the calculated initial rate, and (e) the uncertainty in the calculated initial rate. The horizontal error bars in (d) and (e) represent the size of the bins used for grouping data, whilst the vertical error bars indicate the standard deviation calculated between the 14 unique data sets. The data sets listed are in order: (1) Yang et al., 2019 23, (2) Yang et al., 2001 24, (3 and 4) Liu and Shen, 2008 25, (5) Zhu et al. 2016 26, (6) Yang et al. 2019 27, (7) Yang et al. 2019 28, (8) Mohamed et al. 2007 29, (9) Drenkova-tuhtan et al. 2015 30, (10) Liu et al. 2016 31, (11) Ornek et al. 2007 32, (12) Zhan et al. 2018 33, (13) Ai et al. 2020 34, (14) Nadiye-tabbiruka and Sejie 2019 35.

### Determining the influence of C0 and Cs upon the rate of adsorption and the PSO rate constant k2

The influence of C0 and Cs upon the initial rate of adsorption (calculated as the rate at t=0 using non-linear PSO kinetics) is presented in Figure *2*. For each data set, the order of reaction was determined from the slope of log(initial rate) versus log(C0) or log(Cs) (Figure *2*a,b). Based upon the evaluation of uncertainties in the initial rates calculated using non-linear PSO kinetics (see previous section), the reaction orders are accurate to the nearest integer value. The data sets tend to show a first-order dependency of initial rate upon the initial adsorbate concentration (C0) (Figure *2*c), with an average dependency and standard deviation of 0.80 ±0.38, and a median value of 0.67. Of the 9 data sets, 7 were closest to first-order dependency, whilst 2 were closer to zero-order dependency. The sum of normal distributions representing the reaction orders and uncertainties calculated for each data set was approximated by a single normal distribution. (However, a larger number of data sets are needed to confirm this). Based upon the standard deviation and assuming a normal distribution in the results, the relationship between the initial rate and C0 is first-order with a 90% confidence interval (1.65 standard deviations). This is intuitive for both diffusion and adsorption-controlled mechanisms, as twice as much adsorbate should lead to twice as much adsorbate flux from the surface of the adsorbent into its pores, and collisions with the adsorbent surface should be twice as frequent 36 9.

A first-order dependency of initial rates (normalised to mg L-1 min-1) with respect to the adsorbent concentration (Cs) is also observed (Figure *2*d), albeit with a wider distribution of results: an average value of 1.11 ±0.33 and a median of 1.07. Of the 8 data sets, 6 were closest to first-order dependency, with 1 data set closer to zero-order and another closer to second-order. Based upon the standard deviation and assuming a normal distribution in the results, the relationship between the initial rate and Cs is also first-order with a 90% confidence interval (1.65 standard deviations). This is again intuitive for both diffusion and adsorption-controlled mechanisms, as when Cs is doubled the total surface area available to the solution (m2 L-1) is doubled, the overall flux of adsorbate entering adsorbent pores is doubled, and the rate of collisions between adsorbate and the total adsorbent surface is also doubled. When normalised to mass (mg g-1 min-1) the initial rate is zero-order with respect to Cs, as expected.

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| (a) | (b) |
| (c) | (d) |

Figure 2: Determining the influence of initial adsorbate concentration (C0) and adsorbent concentration (Cs) on the initial rate of adsorption using literature data sets. The order of reaction was determined from the slope of log(initial rate) as a function of (a) log(C0) and (b) log(Cs), with each data point representing a single kinetic experiment (with unique values of C0 and Cs). All experiments in a given data set (one literature paper, where all experimental conditions except for either C0 or Cs are constant) are grouped by colour and symbol, with oxyanions in red, metal cations in blue, and organic dyes in yellow (a legend referencing the literature sources is presented in SI Figure S2). Uncertainties were calculated from the standard error in the slope. The results are alternatively presented using normal distributions with the mean given by the slope and the standard deviation given by the standard error of the slope (c and d). Here, each data set is represented by a dotted line, and the sum of all data sets given by the dashed line. Solid black lines represent the normal distribution obtained by the average of all data sets.

For both predictive modelling and the comparison of adsorption kinetics between literature sources, it is necessary that rate constants are not affected by the experimental conditions. Whilst adsorption kinetics are typically first-order with respect to C0, the PSO rate constant k2 is inversely proportional to C0 (Figure 3a). Consequently, whilst doubling the initial adsorbate concentration typically increases the initial rate of adsorption by a factor of two, counter-intuitively the PSO rate constant k2 will decrease by a factor of two. The average slope of log(k2) versus log(C0) is -0.73±0.46. The inverse relationship between k2 and C0 is explained by the second-order dependence of the PSO model upon the **absolute** concentration of available adsorption capacity remaining through the term (qe-qt)2. In cases where the adsorbent is unsaturated, increasing C0 by a factor of two will approximately double qe. The parameter (qe-qt)2 at t=0 will increase by a factor of four, and consequently k2 must decrease by a factor of two to achieve the doubling of initial rates that is observed (Figure *2*a).

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| (a) | (b) |

Figure 3: Dependence of the pseudo-second order (PSO) rate constant k2 upon (a) initial adsorbate concentration (C0), and (b) adsorbent concentration (Cs). The data is presented as described in Figure 2, with a legend referencing the literature sources presented in SI Figure S2.

In contrast, a positive relationship between Cs and k2 is observed, with an average dependency of 1.57±0.85 (Figure 3b). (First and second-order dependencies between k2 and Cs are both included within the standard deviation). This is explained by how when Cs is doubled, qe will decrease by a factor of between 0 and 2: zero when the adsorbate is in excess and qe is insignificant compared to C0, and two when the adsorbent is in excess and qe is large relative to C0. Consequently, as Cs increases, (qe-qt)2 decreases with a zero-to-second-order dependency, and to achieve the zero-order relationship between C0 and initial rates (with the units mg g-1 min-1), k2 must increase with a dependency that is between zero and second-order.

## Revision of the pseudo-second order (PSO) rate equation to account for changes in adsorbate (C0) and adsorbent (Cs) concentrations

### Modification of the PSO rate equation

In this section, we modify the original PSO rate equation to include the appropriate sensitivity towards C0 and Cs, meeting the aims of (a) improving the predictive capacity of this model, and (b) normalising rate constants for better comparison across the literature.

Firstly, for a given concentration of adsorbent, the total concentration of adsorption surface sites is constant regardless of the value of C0. The term within the rate equation used to represent the contribution of adsorption surface site availability towards the rate of reaction should therefore be independent of C0. The original PSO rate equation contains a second-order dependence upon the **absolute amount** of adsorption capacity remaining, (qe-qt)2, which gives the inverse relationship between the rate constant and C0 demonstrated in Figure 3a. This term can be replaced with a second-order dependence upon the **relative amount** of adsorption capacity remaining, , which will return a value of 1 at time t=0, independent of C0. This term therefore describes the contribution of adsorption surface site availability towards the rate of adsorption more appropriately than the original PSO term (qe-qt)2. Here, is the same as the parameter θ used in the Langmuir adsorption isotherm model 20. This modification of Equation 1 gives the following:

Equation 8

where .

The first-order dependence of the reaction rate upon the adsorbate concentration observed experimentally (Figure *2*c) is then defined within the rate equation, giving:

Equation 9

where . The rate constant k’ takes the units L g-1 min-1.

The initial rate of adsorption tends to be zero-order with respect to Cs (when normalised to adsorbent mass with the units mg g-1 min-1). The original PSO model gives an initial rate that varies with changes in Cs due to its second-order dependence upon the absolute adsorption capacity remaining, through the term (qe-qt)2, and the decrease in qe with increasing Cs. In contrast, since the rPSO equation depends upon the relative adsorption capacity remaining through the term , this rate equation gives the zero-order dependence of initial rates upon Cs that is identified from analysis of the literature. The rPSO rate constant k’ is therefore theoretically independent of changes in Cs, unlike the original PSO rate constant k2. The rPSO model is similar to the adsorption-only form of the kinetic Langmuir model (kLm), which at high surface coverage is first-order with respect to Ct and second-order to ) 37 38.

### Validation of the rPSO rate equation

The removal of experimental conditionality, i.e. the dependency upon C0 and Cs, from the revised model was verified using experimental data from the literature. The ideal rate constant is unaffected by the experimental conditions, and subsequently the dependency of the rate constant with respect to C0 and Cs should be zero. These dependencies were calculated from the slope of log(rate constant) versus log(C0) or log(Cs). As highlighted by Figure 4a, the original PSO rate constant k2 is strongly dependent upon the experimental conditions, being inversely proportional to C0 and second-order with respect to Cs. The average C0 dependency is -0.73±0.46, and the average Cs dependency is 1.57±0.79. In contrast, k’ is approximately zero-order with respect to both experimental variables. Furthermore, the dependencies of k’ upon C0 and Cs vary less (there is less scattering) than k2. The average C0 dependency is -0.20±0.38 and the average Cs dependency is 0.10±0.45. These results demonstrate that the new rate constant k’ is less conditional than k2, and that the dependency of adsorption kinetics upon C0 and Cs is captured by the new model.

When the adsorbate is in excess (qe<C0) the rPSO model approximates the form of the original PSO model. At higher qe values relative to C0, the graphical form of the two models deviates, with reaction rates decreasing more rapidly in the rPSO model due to the parameter Ct decreasing with consumption of the adsorbate. (However, this effect is logical, given that at low Ct values, the rate of adsorption will be limited by the availability of adsorbate). Therefore, rate constants for the rPSO model (k’) can be readily calculated from PSO parameters k2 and qe when the adsorbate is in excess, using the formula . When the adsorbent removes the majority of the adsorbate, however, the rPSO model will require re-fitting due to increasing differences in the graphical form of the PSO and rPSO models.

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| --- | --- |
| (a) | (b) |

Figure 4: Verifying that experimental conditionality (with respect to C0 and Cs) is decreased in the rPSO model versus the original PSO model. (a) The dependencies of the original PSO rate constant k2 and the rPSO rate constant k’ upon C0 and Cs were calculated from the slope of log plots, as per Figure 3, with the ideal rate constant giving a reaction order or ‘dependency’ of zero. The data is shown as normal distributions with the mean and standard deviation set equal to the slope and standard error of the slope in the log plots (with 9 data sets for C0 and 8 for Cs). These values are: -0.73±0.46 for k2 and C0; 1.57±0.79 for k2 and Cs; -0.20±0.38 for k’ and C0; 0.10±0.45 for k’ and Cs. (b) A comparison of the forms of the original PSO and rPSO models, with different ratios (with Cs=1 g L-1). The original PSO model is presented in blue and the rPSO model in red, with equal to 1 (dotted lines), 2 (dashed lines), and 5 (solid lines).

## Example applications

### Application 1: Improved predictive capabilities using the revised PSO model

The first objective of this work was to provide a simple modification of the popular PSO model to introduce predictive capabilities, for the purpose of engineering studies 39. If the kinetic model is to be used to predict adsorption performance under different conditions, then it is essential that the model parameters obtained experimentally are valid in a range of scenarios. Consequently, we evaluated whether the rPSO model would provide a better fit to experimental data compared against the PSO model, if a single rate constant is used to model multiple experiments with different values of C0 and Cs.

The original PSO model tends to systematically overestimate qt for experiments with high C0­ or low Cs values and systematically underestimate qt for experiments with low C0 or high Cs values (Figure 5). This is due to the negative and positive relationships between k2 and C0 and Cs respectively as previously discussed, with this relationship being denied when a single value of k2 is used to model all experiments. The rPSO model gives a better fit to experimental data (i.e. a smaller sum of squared residuals) in 5 of the 6 data sets tested (all panels in Figure 5 except d). The median value of the sum of squared residuals decreased by 66% when changing from the PSO model to the rPSO model.

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| (a) | (b) |
| (c) | (d) |
| (e) | (f) |

Figure 5: Application study 1: Using the revised PSO (rPSO) model (solid lines) to describe multiple experiments with a single rate constant, compared against the original PSO model (dotted lines). (a,b,c) present 3 experiments where C0 is varied, and (d,e,f) present 3 experiments where Cs is varied. Experimental data was collected from Manna et al. (2003) 40, Singh et al. (1996) 41, Mezenner and Bensmaili (2009) 42, Debnath et al. (2017) 43, Lazaridis et al. (2004) 44, and Shipley et al. (2013) 45.

The average relative error of qt calculated by the rPSO model is just 1±17%, versus -11±27% for the original PSO model (Figure 6a), indicating that the rPSO model provides greater accuracy when modelling adsorption kinetics with changing values of C0 and Cs using a single rate constant. Furthermore, the cross-calibration curve of q­t values (modelling versus experiment) is significantly closer to the ideal one-to-one line when using the rPSO model, with an R2 value of 0.9999 versus just 0.9217 for the original PSO model (Figure 6b). Considering each experimental data series in turn, the typical slope of the calibration curve was closer to one, with less scattering, in the rPSO model (a slope of 0.99±0.11) compared against the original PSO model (with a slope of 1.23±0.35) (Figure 6c).

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|  | (a) | |  |
| (b) | | (c) | |

Figure 6: Application study 1: Cross-calibration of the rPSO model against experimental data (6 literature sources, 22 experiments and 198 data points). (a) Box and whisker plot presenting the relative error of qt calculated via the original PSO model and the rPSO model. The boxes highlight the 25%, 50% (median) and 75% percentiles, whilst the whiskers represent the minima and maxima excluding ‘outlier’ data points, defined as those greater than the top of the box plus 1.5 times the interquartile range, or less than the bottom of the box minus 1.5 times the interquartile range. (b) Cross-calibration plot highlighting the goodness of fit against the one-to-one line. Open shapes indicate qt values calculated using the original PSO model, whilst filled shapes indicate the rPSO model. Values of R2 indicate the goodness of fit against the ideal one-to-one line. (c) Comparison of the cross-calibration slopes with each model and each data set. Literature sources are denoted as As(III)/HFO 40 (dark blue squares), As(V)/Fe2O3 41 (light blue circles), HPO42-/iron hydroxide 42 (dark green diamonds), Cr(VI)/Fe2O3 43 (light green triangles), Cr(VI)/Mg-Al-CO3 44 (orange squares), and Cd(II)/Fe2O3 45 (red circles). Further results are presented in SI Figure S3.

Whilst the rPSO rate constant k’ appears to be more stable to changes in experimental conditions than the PSO rate constant k2, the parameter qe is conditional, depending upon C0 and Cs. For predictive modelling, this limitation can be rectified by using an adsorption isotherm to predict qe (such as the Langmuir or Freundlich model 46). Though a single value of qe can be determined for the entirety of each experiment, in scenarios such as a column reactor the equilibrium adsorbate concentration parameter Ce has diminished physical significance, and it may be better to replace this term with Ct, recalculating the hypothetical value of qe at each point in time. Huang and co-workers previously demonstrated that this approach can give a better account of the true driving force of the reaction during the initial stages of adsorption 47.

### Application 2: Comparison of rate constants between different experimental studies

The rPSO rate constant k’ is expected to be more meaningful and more appropriate than k2 when comparing adsorption kinetics reported in the literature since k’ is less sensitive towards experimental conditions (C0 and Cs) in than k2. To demonstrate the potential application of normalised rate constants towards achieving a meaningful comparison of adsorption kinetics reported in the literature, we collected 14 and 7 literature sources reporting the kinetics of inorganic arsenic As(V) and As(III) adsorption onto iron oxide and alumina adsorbents respectively.

The average value of log(k2) for all iron oxide studies is -0.93±1.50, whilst the average of log(k’) is -1.05±1.08. In both cases, the standard deviation is significant, with more than an order of magnitude variation in k2 and k’ values: neither model provides a rate constant that is valid for different iron oxide adsorbents used in different studies. Similarly, the adsorption of inorganic arsenic onto alumina gives average values of log(k2) = 0.98±1.84 and log(k’) = 0.35±1.75.

Whilst the variation in both k2 and k’ across the literature is large, the influence of adsorbent morphology on adsorption kinetics has not been incorporated into either of the PSO and rPSO models. Adsorption kinetics are often faster for adsorbent materials with smaller particles, due to the improved rate of mass transport bringing the adsorbate to the adsorbent surface sites 48. For instance, the intraparticle diffusion model gives a rate of adsorption that is proportional to r-1 (where r is particle size) 49.

Whilst a faster reaction is anticipated for small iron oxide particle sizes, plotting log(k2) as a function of log(r-1) shows a weak inverse relationship (linear regression gives a slope of -0.49±0.20 and R2=0.3234) (Figure 7a). This is due to the significant increase in qe as the particle size decreases (SI Figure S4) and the inverse relationship between k2 and qe through the term (qe-qt)2 as previously discussed. Since adsorption onto smaller particles is typically faster than onto larger particles, the comparison of k2 values for different adsorbent sizes and different adsorbent materials (i.e. iron oxides versus alumina) is not useful and is likely to lead to false conclusions.

In contrast, we see the anticipated positive relationship for log(k’) as a function of log(r-1) for both iron oxide and alumina adsorbents (Figure 7b). The iron oxides show a slope of 0.44±0.1 with R2=0.5211, and alumina shows a slope of 0.62±0.25 and R2=0.5547. This suggests that the rPSO rate constant k’ captures the influence of particle size on adsorption kinetics. The limited goodness of fit in the linear regression is controlled by factors including poor characterisation of the particle size and differences in experimental conditions beyond C0 and Cs, such as the pH. The accurate characterisation of particle size is especially challenging, given the range of techniques used by the literature including transmission electron microscopy (TEM), dynamic light scattering (DLS) and sieve fractionation.

The results from this literature survey show greater log(k’) values at each specific particle size for alumina versus iron oxides, suggesting that the adsorption of inorganic arsenic is faster onto alumina than onto iron oxides. With more rigorous analysis, such a study would have important implications in the design of engineered solutions for arsenic remediation, i.e. opting to use alumina in place of iron oxides in a packed column when larger particle sizes and high flow rates are required. This highlights that normalisation of the PSO rate constant k2 to the rPSO rate constant k’, or some other constant, can achieve a more meaningful comparison of the adsorption kinetics reported by the literature.

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| (a) | (b) |

Figure 7: Application study 2: Use of the rPSO rate constant k’ to compare literature sources with adsorption kinetics determined under different experimental conditions. Particle size decreases from left to right. Presented are As(V) (red filled shapes) and As(III) (orange filled shapes) adsorption onto iron oxides, and As(V) (dark blue open squares) and As(III) (light blue open circles) adsorption onto alumina. Each data point indicates a different literature source, with a legend given in SI Figure S5.

# Conclusions

This work aimed to modify the popular pseudo-second order (PSO) model of adsorption kinetics to remove experimental conditionality, focusing upon initial adsorbate concentration (C0) and adsorbent concentration (Cs). A revised PSO rate equation (rPSO) was developed from the empirical analysis of 64 kinetic experiments taken from 15 literature sources. The final equation takes the form . The first application study demonstrates that the rPSO equation allows for a single rate constant to model multiple experiments, differing in experimental conditions C0 and Cs, with greater accuracy and a 66% decrease in the sum of squared residuals versus the original PSO model. The second application study demonstrates that the rPSO equation provides a rate constant which is more useful for comparison across the literature than the PSO rate constant k2, obeying the anticipated relationship between adsorption rates and particle size.

The new rate equation is similar to an adsorption-only form of the kinetic Langmuir model (kLm), which at high surface coverage is first-order with respect to Ct and second-order with respect to ) 37 38. However, the rPSO equation is simpler, with fewer fitting parameters needed, and may thus be more useful for the non-expert. The rPSO equation may prove more useful than the original PSO model in engineering studies where operating conditions are likely to vary.

One of the reasons for the popularity of the original PSO model is its linearised forms, from which k2 and qe parameters can be readily obtained from experimental data. Whilst we have unfortunately not yet found a way to linearise the rPSO rate equation, it is worth noting that linearisation of the original PSO model often results in a poorer quality of fit versus when using non-linear fitting 14. Where necessary, the rate constant for this revised model can be quickly obtained from linearised PSO kinetics using the expression .

In our analytical approach, we demonstrate that non-linear fitting of PSO kinetics is more appropriate than linearised PSO kinetics and the initial slope approach when early kinetic data is limited, as is often the case in adsorption experiments. Our literature survey only yielded 9 data sets where C0 was varied and 8 where Cs was varied, satisfying our requirements for early kinetic data with . This highlights a need for experimental work to investigate the influence of these independent variables more systematically, and to ensure that initial adsorption kinetics are adequately captured, given that the method of initial rates is typically considered the superior approach towards determining reaction orders 17.

# Acknowledgements

The authors acknowledge support from the Engineering Physical Sciences Research Council (EPSRC) [grant number EP/N509486/1].

# Supporting information

The supplementary information provides references to all data sets used in this work; a fuller comparison of the three mathematical approaches used to calculated initial rates; and supporting figures regarding the two application studies.

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