

A Revised Pseudo-Second-Order Kinetic Model for Adsorption, Sensitive to Changes in Adsorbate and Adsorbent Concentrations

Jay Bullen, Sarawud Saleesongsom, Kerry Gallagher, Dominik Weiss

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2	A revised pseudo-second order kinetic model for adsorption,
3	sensitive to changes in adsorbate and adsorbent
4	concentrations
5	
6	^{1*} Jay C. Bullen; ¹ Sarawud Saleesongsom; ² Kerry Gallagher; and ^{1,3*} Dominik J. Weiss
7	
8	¹ Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, United Kingdom
9	² Géosciences/OSUR, University of Rennes, Rennes, 35042, France
10	³ Civil and Environmental Engineering, Princeton University, United States of America
11	
12	
13	*Corresponding authors:
14	Email: j.bullen16@imperial.ac.uk; d.weiss@imperial.ac.uk
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17	Graphical Abstract
	original PSO model $\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ $\int_{\mathbf{revised}} \operatorname{PSO model}$ $\frac{dq_t}{dt} = k'C_t \left(1 - \frac{q_t}{q_e}\right)^2$ $(R^2 = 0.9999)$ • new model $\stackrel{\bullet}{\longrightarrow} \stackrel{\bullet}{\longrightarrow} \stackrel{\bullet}{\longrightarrow}$
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20	Keywords
21	Adsorption kinetics; kinetic model; pseudo-second order; Lagergren; water treatment; particle size

Abstract

23 The development of new adsorbent materials for the removal of toxic contaminants from drinking 24 water is crucial to achieving the United Nations Sustainable Development Goal 6 (clean water and 25 sanitation). The characterisation of these materials includes fitting models of adsorption kinetics to 26 experimental data, most commonly the pseudo-second order (PSO) model. The PSO model, 27 however, provides no sensitivity to changes in experimental conditions such as adsorbate and 28 adsorbent concentrations (C_0 and C_s) and consequently is not able to predict changes in performance 29 as a function of operating conditions. Furthermore, the experimental conditionality of the PSO rate 30 constant, k₂, can lead to erroneous conclusions when comparing literature results. In this study, we 31 analyse 108 kinetic experiments from 47 literature sources to develop a relatively simple 32 modification of the PSO rate equation, yielding:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \mathrm{k}'\mathrm{C}_{\mathrm{t}}\left(1 - \frac{\mathrm{q}_{\mathrm{t}}}{\mathrm{q}_{\mathrm{e}}}\right)^{2}$$

33 Unlike the original PSO model, this revised rate equation (rPSO) demonstrates the first-order and 34 zero-order dependencies upon C_0 and C_s that we observe empirically. Our new model reduces the 35 residual sum of squares by 66% when using a single rate constant to model multiple adsorption 36 experiments with varying initial conditions. Furthermore, we highlight how the rPSO rate constant k' 37 is more appropriate for literature comparison, highlighting faster kinetics in the adsorption of 38 arsenic onto alumina versus iron oxides. This revised rate equation should find applications in 39 engineering studies, especially since unlike the PSO rate constant k_2 , the rPSO rate constant k' does 40 not show a counter-intuitive inverse relationship with the increasing reaction rate when C_0 is 41 increased.

42 Introduction

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44 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, 45 ease of separation from the effluent²³, or multifunctional capabilities such as photocatalytic activity 46 ⁴⁵. Energy input typically forms about one third of water treatment plant operation costs ⁶, and if 47 48 energy efficiencies are to be improved then accurate models of adsorption kinetics (including rate constants) are needed to (a) identify the minimum duration needed for batch treatments and (b) 49 estimate maximum flow rates for column or continuous-flow treatments⁷. Laboratory experiments 50 can only partially capture the environments in which new adsorbents will operate, and in practice 51 52 different concentrations of adsorbent (C_s) will be needed to treat different concentrations of 53 contaminant in the influent (C_0). It is thus important that adsorption models are made sensitive to 54 operating conditions, providing predictive capabilities.

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

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

Equation 1

59 where t is time (minutes), q_t is the amount of adsorbate adsorbed per mass of adsorbent at time t 60 (mg g⁻¹), k_2 is the pseudo-second order rate constant (g mg⁻¹ min⁻¹), and q_e is the amount of 61 adsorbate adsorbed at equilibrium (mg g⁻¹)⁹.

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

$$C_t = C_0 - C_S q_t$$

Equation 2

64 where C_t is the concentration of aqueous adsorbate at time t (mg L⁻¹), C_0 is the initial adsorbate 65 concentration at t=0 (mg L⁻¹) and C_s is the concentration of adsorbent (g L⁻¹).

66 The PSO model is popular for several reasons. Firstly, it has a simple mathematical form. Secondly, 67 despite being applied by Ho and McKay as a mechanistic model for the bidentate adsorption of 68 copper onto peat ¹¹, the PSO model is able to fit kinetic data for a wide range of systems with 69 different reaction mechanisms ^{9 12 13} (including where diffusion control is to be expected ¹⁴). Thirdly, 70 Equation 1 can be integrated and rearranged to provide linear equations (of the form y=mx+c) from 71 which the model parameters k₂ and q_e can be easily obtained by linear regression ¹⁵.

However, the PSO model has several important limitations due to the absence of adsorbate and adsorbent parameters within the rate equation, with k_2 and q_e parameters being valid only under the specific 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 C_0 and C_s , limiting its application 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 possessing superior adsorption kinetics.

79 The aim of the present study was to modify the popular PSO equation, introducing sensitivity 80 towards changes in C_0 and C_s , with the objective of both improving predictive capabilities for 81 engineering studies, and normalising rate constants for easier comparison between literature 82 sources. 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 83 similarly to develop an empirical model, rather than a mechanistic model. We thus conducted an 84 85 empirical analysis of the adsorption kinetics reported by the literature to assess the influence of C_0 and C_s on adsorption rates, and to modify the PSO rate equation accordingly. 86

We used the method of initial rates to determine the order of reaction with respect to both C₀ and C_s 87 (given the possibility for data at later times to disguise the true reaction order ¹⁷, such as when 88 slower surface precipitation processes coincide with monolayer adsorption ¹⁸). We first performed 89 90 quality control experiments, investigating various methods for calculating initial rates when the 91 availability of early kinetic data is limited (as per many adsorption experiments). We then compiled a 92 wide range of literature data sets wherein multiple adsorption kinetic experiments with different 93 values of C₀ and C_s are reported (with each data set being a specific adsorbate-adsorbent system) 94 and determined the order of reaction with respect to each variable. We used mineral and organic 95 adsorbents, and metal, inorganic and organic adsorbates, to achieve a model that is generally 96 applicable to a wide range of systems, as per the original PSO model. We built the observed C₀ and 97 Cs dependence into a revised form of the PSO rate equation (which we refer to as rPSO) and verified 98 that the rate constants given by this new model are more stable with respect to changes in 99 experimental conditions than the PSO rate constant k_2 . Finally, we used two application studies to 100 assess the potential of this revised PSO model to overcome current limitations: (1) describing multiple experiments with varying values of C_0 and C_s using a single rate constant, and (2) achieving a 101 102 more meaningful comparison of the adsorption kinetics reported across the literature.

103 **Experimental**

104

105 Data sets

Literature sources that experimentally investigated the influence of C_{0} , C_{s} or particle size upon 106 adsorption kinetics were compiled and the experimental data tabulated (referenced in the 107 108 Supplementary Information: SI Table S1). Both mineral adsorbents and organic adsorbents (activated 109 carbon and chitosan) were included, however zeolites and metal-organic frameworks (MOFs) were 110 not since the sorption mechanism of adsorbate trapping within cages might produce contrary 111 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, C_s or particle 112 113 size. 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 114 includes: 14 literature sources with early kinetic data (where $0 < \frac{q_t}{q_e} < 0.2$) to investigate the 115 influence of early data availability on calculations of the initial rate; 8 literature sources (9 data sets) 116 with a total 37 experiments where C₀ is varied; 6 literature sources (8 data sets) with a total 27 117 experiments where C_s is varied; and 21 literature sources (25 experiments) for the adsorption of 118 inorganic arsenic onto iron oxide and alumina adsorbents. A data set is considered to be all kinetic 119 experiments using the same adsorbate-adsorbent system within a single literature source. The 120 121 compiled data sets are available elsewhere ¹⁹.

122

123 Mathematical approaches for the determination of initial rates

124 Three approaches towards the calculation of initial rates were compared: (1) the initial slope, (2) 125 linearised PSO kinetics, and (3) non-linear PSO kinetics.

126 In the initial slope approach, the initial rate $\left(\frac{\Delta q_t}{\Delta t} \text{ at } t=0\right)$ was calculated as the slope between the 127 origin at (0,0) and the earliest available data point at t>0²⁰.

128 Initial rates were also calculated using the following linearised form of the integrated PSO rate 129 equation:

$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{k}_2 \mathrm{q}_{\mathrm{e}}^2} + \frac{\mathrm{t}}{\mathrm{q}_{\mathrm{e}}}$$

130

131 Kinetic profiles were plotted as $\frac{t}{q_t}$ as a function of t and the linear regression was obtained using the 132 LINEST function in Excel (where the residual sum of squares between the data points and the linear 133 regression is minimised). The equilibrium adsorption parameter q_e was obtained via the relationship 134 $q_e = \frac{1}{m}$ where m is the slope of the linear regression, and k_2 via $k_2 = \frac{1}{c \cdot q_e^2}$ where c is the y-intercept. 135 The initial rate of adsorption was then calculated through the simplification of Equation 1:

136 Initial rate =
$$\frac{dq_{t=0}}{dt} = k_2 q_e^2$$

Equation 3

Equation 4

- 138 Uncertainties in k_2 , q_e and the initial rate were calculated by linear propagation of the standard 139 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 k_2 and q_e values, minimising the sum of squared residuals between the model and experiment. Uncertainties in k_2 and q_e were calculated using a Monte-Carlo approach with 200 simulations as described by Hu
- 144 et al.²¹.

For all literature sources, parameters were recalculated to the same units for ease of comparison: k_2 (g mg⁻¹ min⁻¹); q_e (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 147 calculated using these three approaches was evaluated as follows. Fourteen data sets containing 148 early kinetic data were collected (defined as adsorption experiments containing data within the 149 range $0 < \frac{q_t}{q_e} < 0.2$). Initial rates were then re-calculated as data points were consecutively removed 150 from the earliest to the latest. A linear regression between the calculated initial rates and the value 151 of $\frac{q_t}{q_e}$ at the first available kinetic data was determined and extrapolated to $\frac{q_t}{q_e} = 0$ to provide a 152 theoretical 'true' initial rate (representing if kinetic data were to be collected within an 153 154 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. 155 A systematic error was calculated using the average error across all data sets and a random error 156 was calculated as the standard deviation in the error across all data sets. The significance of the 157 158 differences observed in the initial rate errors given by the three mathematical approaches was 159 determined using the paired samples t-test.

160 After evaluating the three approaches (see Results and Discussion), non-linear PSO kinetics were 161 used to determine initial rates in all subsequent calculations.

162

163 Determining the order of reaction

164 The order of reaction with respect to the independent variables C_0 and C_s was calculated as the slope 165 of log(initial rate) versus log(independent variable) ²². The order of reaction was calculated for each 166 data set (kinetic experiments using the same adsorbate-adsorbent system within a single literature 167 source), with each data point used within the linear regression representing a single kinetic 168 experiment at a unique value of C_0 or C_s . This is represented by the equation:

order of reaction =
$$\frac{\Delta \log (\text{initial rate})}{\Delta \log (C_0 \text{ or } C_s)}$$

169

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 error for each data set was specified as the standard error of the slope. An average (mean, \bar{x}) order of reaction representing all data sets was

Equation 6

Equation 7

- 173 calculated, with errors reported as the standard deviation. The dependencies of k_2 and k' upon C_0 174 and C_s were determined using the same method, only substituting the initial rate with k_2 or k'.
- 175

176 Modelling the revised rate equation

Our final rate equation, developed and derived in the Results and Discussion (Equation 11, referredto as the rPSO), is:

$$\frac{dq_t}{dt} = k'C_t \left(1 - \frac{q_t}{q_e}\right)^2$$

179

180 where the rate constant k' takes the units $L g^{-1} min^{-1}$. As the rPSO rate equation is not easily 181 integrated, experiments were simulated using Microsoft Excel. The quantity of adsorbate adsorbed 182 at the nth data point was calculated using the following formula:

$$q_n = q_{n-1} + \left((t_n - t_{n-1}) \cdot \left(k' C_{t(n-1)} \left(1 - \frac{q_{n-1}}{q_e} \right)^2 \right) \right)$$

183

184 The time interval between data points, $(t_n - t_{n-1})$ or Δt , was reduced until the magnitude of Δt had 185 no significant effect on the results. The rPSO parameters k' and q_e were obtained by non-linear 186 fitting, using Microsoft Excel's Solver function to minimise the residual sum of squared residuals 187 between the model and experiment.

For all literature sources, parameters were recalculated to the same units for ease of comparison: k_2 (g mg⁻¹ min⁻¹); q_e (mg g⁻¹); and the initial rate (mg g⁻¹ min⁻¹).

190

192

197

191 KERRR

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

Equation 8

where t is time (minutes), q_t is the amount of adsorbate adsorbed per mass of adsorbent at time t (mg g⁻¹), k_2 is the pseudo-second order rate constant (g mg⁻¹ min⁻¹), and q_e is the amount of adsorbate adsorbed at equilibrium (mg g⁻¹)⁹.

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

$$C_t = C_0 - C_S q_t$$

Equation 9

- where C_t is the concentration of aqueous adsorbate at time t (mg L⁻¹), C_0 is the initial adsorbate concentration at t=0 (mg L⁻¹) and C_s is the concentration of adsorbent (g L⁻¹).
- 200 KERRR

202 Application studies

203 In the first application study (evaluating the potential of the rPSO model for predictive applications), 6 data sets were used: 3 where C₀ was varied and 3 where C_s was varied. In the first step, values of 204 205 the equilibrium adsorption capacity (qe) to constrain the model were obtained by fitting kinetic 206 experiments individually using the PSO and rPSO models (optimising the rate constant and qe 207 simultaneously to minimise the sum of squared residuals). After constraining qe to these values, all 208 experiments within the given data set (i.e. experiments with the same adsorbate-adsorbent system 209 but different C_0 or C_s values) were simultaneously fit with the PSO and rPSO models, using a single rate constant (k₂ or k', depending upon the model) to describe all experiments. 210

- 211 In the second application study (evaluating the potential of the rPSO rate constant k' for more
- 212 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
- 216 comparison. The particle radius (r) was taken as reported by each study.

217 Results and Discussion

218

219Determination of the influence of experimental conditions (C₀ and C_s) on the220initial rate of adsorption

221

222Quality control: The calculation of initial rates and setting criteria for the selection223of literature data sets

224 Many adsorption experiments reported by the literature begin their collection of kinetic data at high 225 values of $\frac{q_t}{q_e}$, 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

228 lack of appreciation over the time-scale at which adsorption kinetics are best measured, with many

- papers fitting kinetic models on timescales when the reaction has already plateaued and reachedequilibrium.
- 231 Whilst we chose to investigate the influence of C_0 and C_s using the method of initial rates, the lack of
- 232 literature reporting early stage kinetic data (i.e. low values of $\frac{q_t}{q_e}$) 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, creating a systematic underestimation of the initial rate. In the most extreme case, an infinite delay before collection of kinetic data will yield a slope of zero and subsequently an initial rate of zero. 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

239 upon how closely the experimental data obeys the applied 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 within the investigation of the influence of C_0 and C_s on adsorption kinetics.

The literature search identified fourteen data sets satisfying the criteria that $\frac{q_t}{q_o} < 0.2$, a relatively 246 small number, highlighting how most authors fail to collect early kinetic data (SI Figure S1). Initial 247 248 rates calculated from the slope between the origin and the earliest available data point show the 249 typical systematic underestimation of initial rates when early kinetic data is missing (Figure 1a, with 250 the solid line representing the average of all data sets). In contrast, when calculated using the PSO 251 model, there is no systematic error in the calculation of initial rates when the first kinetic data is collected in the range $0 < \frac{q_t}{q_e} < 0.7$ (Figure 1b,c). In all three approaches, significant variation 252 between data sets is observed, i.e. an error in the initial rate unique to each data set. This error (with 253 254 dashed lines representing one standard deviation) is approximately constant in the initial slope 255 approach, being significant even when early kinetic data is available. In contrast, this error is insignificant using early kinetic data and either of the PSO approaches, however this error increasesin magnitude as early data is sequentially removed.

- 258 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 259 260 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 261 262 using non-linear PSO kinetics versus linearised PSO kinetics is not significant (p=0.33 using the 14 263 initial rate calculations). However, when comparing the calculated initial rates with all possible data 264 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 265 biased weighting of linearised PSO kinetics towards data at later times, with the slope of $\frac{t}{a}$ versus t 266 increasing as equilibrium adsorption is approached, returning smaller values of qe and thus giving a 267 268 smaller initial rate. The difference between initial rates calculated using linearised and non-linear 269 PSO kinetics was observed despite equilibrium adsorption kinetic data from the original literature 270 being excluded in our calculations.
- 271 Finally, we considered the uncertainties in the initial rates calculated using the two PSO approaches 272 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 273 regression fit to $\frac{t}{q_r}$ versus t, whilst the uncertainties in non-linear PSO kinetics were calculated using 274 synthetic data and 200 Monte-Carlo simulations²¹. Using linearised PSO kinetics, the propagated 275 uncertainty in the initial rate increases exponentially as early kinetic data is removed. This is 276 explained by how late stage adsorption kinetic data is weighted too heavily when fitting linearised 277 PSO kinetics ¹⁰, where the differences in q_t are smaller relative to the measurement uncertainty: this 278 increases the uncertainty of the linear regression. At $\frac{q_t}{q_e} = 0.6$, the average uncertainty in the initial 279 rates calculated using linearised PSO kinetics is 9.5%. In contrast, the uncertainty in the initial rates 280 calculated using non-linear PSO kinetics is essentially independent of the availability of early kinetic 281 data, and at $\frac{q_t}{q_e} = 0.6$ the average uncertainty is only 5.7%. 282
- As highlighted here, ideally the data sets used to explore the influence of experimental parameters 283 such as the adsorbate concentration (C₀) and the adsorbent concentration (C_s) should include early 284 kinetic data to reduce the uncertainty in the calculated initial rates. However, literature data 285 286 reporting early adsorption kinetics is limited. 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, 287 we set the criterion that data sets must include kinetic data with $\frac{q_t}{q_e} < 0.6$. This boundary condition 288 gives an average error in the calculated initial rate of -44 ±22 % for the initial slope approach, +17 289 290 ± 38 % using linearised PSO kinetics, and only +3 $\pm 27\%$ for the non-linear PSO kinetics. The results 291 indicate that non-linear PSO kinetics are most appropriate for calculating initial rates, with an 292 insignificant systematic error. A ~30% uncertainty remains, associated with how closely the 293 adsorption kinetics fit to the PSO form (with deviations being both due to inaccurate measurements 294 and real chemical mechanisms).

295 By considering a literature source reporting two kinetic experiments only, with a different value of C_0 296 or C_s in each, a 30% error in the initial rate of the first experiment (as per the boundary condition of $\frac{q_t}{r}$ < 0.6) will confer an error of <0.5 in the calculated reaction order. In this work, the average value 297 qe of $\frac{q_t}{q_e}$ in the first available kinetic data was 0.37 for experiments where C₀ is varied, and 0.27 for 298 experiments were C_s is varied. Furthermore, the number of kinetic experiments in each literature 299 300 data set was 3-6, indicating that the uncertainties in the calculated initial rates will be <30%. Under these conditions, the calculated orders of reaction will be accurate to the nearest integer value. This 301 302 was deemed appropriate for the purposes of developing the revised PSO model, given that it is 303 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 a similar 304 305 analysis could be made relaxing this condition.

306 Consequently, non-linear fitting of the PSO model was used to determine the initial rate of 307 adsorption in each kinetic experiment in all subsequent work.





309 Figure 1: The influence of the limited availability of early kinetic data on the calculation of initial rates of adsorption, 310 assessed by the analysis of 14 literature sources. The influence of removing early kinetic data on the calculated initial rates 311 was assessed using (a) the initial slope, (b) linearised PSO kinetics, and (c) non-linear PSO kinetics. The theoretical 'true' 312 initial rate is given by initial rate₀ and the initial rate calculated with the available data given by initial rate_i. The solid black 313 line represents the average of the 14 data sets, whilst dotted lines indicate one standard deviation. The three approaches 314 are compared, assessing the influence of data availability on (d) the relative error in the initial rate, and (e) the uncertainty 315 in the calculated initial rate. The horizontal error bars in (d) and (e) represent the size of the bins used for grouping data, 316 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., 2019²³, (2) Yang et al., 2001²⁴, (3 and 4) Liu and Shen, 2008²⁵, (5) Zhu et al. 2016²⁶, (6) Yang et al. 2019²⁷, (7) Yang et al. 2019²⁸, (8) Mohamed et al. 2007²⁹, (9) Drenkova-tuhtan et al. 2015³⁰, (10) Liu et al. 317 318 2016³¹, (11) Ornek et al. 2007³², (12) Zhan et al. 2018³³, (13) Ai et al. 2020³⁴, (14) Nadiye-tabbiruka and Sejie 2019³⁵. 319

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- 321 322

Determining the influence of C_0 and C_s upon the rate of adsorption and the PSO rate constant k_2

The influence of C₀ and C_s upon the initial rate of adsorption (calculated as the rate at t=0 using non-323 linear PSO kinetics) is presented in Figure 2. For each data set, the order of reaction was determined 324 325 from the slope of log(initial rate) versus $log(C_0)$ or $log(C_s)$ (Figure 2a,b). Based upon the evaluation of 326 uncertainties in the initial rates calculated using non-linear PSO kinetics (in the previous section), the 327 reaction orders are accurate to the nearest integer value. The data sets tend to show a first-order 328 dependency of initial rate upon the initial adsorbate concentration (C_0) (Figure 2c), with an average 329 dependency and standard deviation of 0.80 ±0.38, and a median value of 0.67. Of the 9 data sets, 7 330 were closest to first-order dependency, and 2 were closer to zero-order dependency. The sum of 331 normal distributions representing the reaction orders and uncertainties calculated for each data set 332 was approximated by a single normal distribution. (However, a larger number of data sets are 333 needed to verify this). Based upon the standard deviation and assuming a normal distribution in the 334 results, the relationship between the initial rate and C₀ is first-order with a 90% confidence interval 335 (1.65 standard deviations). This is intuitive for both diffusion and adsorption-controlled mechanisms, 336 as twice as much adsorbate should lead to twice as much adsorbate flux from adsorbent surface into pores, and collisions with the adsorbent surface should be twice as frequent ^{36 9}. 337

A first-order dependency of initial rates (normalised to $mg L^{-1} min^{-1}$) with respect to the adsorbent 338 concentration (C_s) is also observed (Figure 2d), albeit with a wider distribution of results: an average 339 340 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 341 342 the standard deviation and assuming a normal distribution in the results, the relationship between the initial rate and C_s is also first-order with a 90% confidence interval (1.65 standard deviations). 343 This is again intuitive for both diffusion and adsorption-controlled mechanisms, as when C_s is 344 doubled the total surface area available to solution (m² L⁻¹) is doubled, the overall flux of adsorbate 345 entering adsorbent pores is doubled, and the rate of collisions between adsorbate and total 346 adsorbent surface is also doubled. When normalised to mass (mg g⁻¹ min⁻¹) the initial rate is zero-347 order with respect to C_s, as expected. 348



350 Figure 2: Determining the influence of initial adsorbate concentration (C_0) and adsorbent concentration (C_0) on the initial 351 rate of adsorption using literature data sets. The order of reaction was determined from the slope of log(initial rate) as a 352 function of (a) $\log(C_0)$ and (b) $\log(C_s)$, with each data point representing a single kinetic experiment (with unique values of C_0 353 and C_s). All experiments in a given data set (one literature paper, where all experimental conditions except for either C_0 or C_s 354 are constant) are grouped by colour and symbol, with oxyanions in red, metal cations in blue, and organic dyes in yellow (a 355 legend referencing the literature sources is presented in SI Figure S2). Uncertainties were calculated from the standard error 356 in the slope. The results are alternatively presented using normal distributions with the mean given by the slope and the 357 standard deviation given by the standard error of the slope (c and d). Here, each data set is represented by a dotted line, 358 and the sum of all data sets given by the dashed line. Solid black lines represent the normal distribution obtained by the 359 average of all data sets.

- 361 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
- 363 kinetics are typically first-order with respect to C₀, the PSO rate constant k₂ is inversely proportional

364 to C_0 (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 365 366 will decrease by a factor of two. The average slope of $log(k_2)$ versus $log(C_0)$ is -0.73±0.46. The inverse 367 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 $(q_e-q_t)^2$. In 368 cases where the adsorbent is unsaturated, increasing C₀ by a factor of two will approximately double 369 q_e . The parameter $(q_e-q_t)^2$ at t=0 will increase by a factor of four, and consequently k_2 must decrease 370 by a factor of two to achieve the observed doubling of initial rates. 371



Figure 3: Dependence of the pseudo-second order (PSO) rate constant k_2 upon (a) initial adsorbate concentration (C_0), and (b) adsorbent concentration (C_s). The data is presented as described in Figure 2, with a legend referencing the literature sources presented in SI Figure S2.

375

In contrast, a positive relationship between C_s and k₂ is observed, with an average dependency of 376 1.57±0.85 (Figure 3b). (First and second-order dependencies between k_2 and C_s are both included 377 378 within the standard deviation). This is explained by how when C_s is doubled, q_e will decrease by a factor of between 0 and 2: zero when the adsorbate is in excess and qe is insignificant compared to 379 380 C₀, and two when the adsorbent is in excess and q_e is large relative to C₀. Consequently, as C_s increases, $(q_e-q_t)^2$ decreases with a zero-to-second-order dependency, and to achieve the zero-order 381 relationship between C_0 and initial rates (mg g⁻¹ min⁻¹), k₂ must also increase with a dependency that 382 383 is between zero and second-order.

Revision of the pseudo-second order (PSO) rate equation to account for
changes in adsorbate (
$$C_0$$
) and adsorbent (C_s) concentrations

388 Modification of the PSO rate equation

In this section, we modify the original PSO rate equation to include the appropriate sensitivity towards C_0 and C_s , meeting the aims of (a) improving the predictive capacity of this model, and (b) normalising rate constants for better comparison across the literature.

392 Firstly, for a given concentration of adsorbent, the total concentration of adsorption surface sites is 393 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 394 395 independent of C₀. The original PSO rate equation contains a second-order dependence upon the **absolute amount** of adsorption capacity remaining, $(q_e-q_t)^2$, which gives the undesirable inverse 396 relationship between the rate constant and C₀ demonstrated in Figure 3a. This term can be replaced 397 398 with a second-order dependence upon the relative amount of adsorption capacity remaining, $\left(1-\frac{q_t}{q_o}\right)^2$, which will always return a value of 1 at time t=0, independent of C₀. This term therefore 399 describes the contribution of adsorption surface site availability towards the rate of adsorption more 400 appropriately than the original PSO term $(q_e-q_t)^2$. Here, $\frac{q_t}{q}$ is the same as the parameter θ used in the 401 Langmuir adsorption isotherm model ²⁰. This modification of Equation 1 gives the following: 402

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

404

405 where
$$k'' = k_2 q_e^2$$
.

406 The first-order dependence of the reaction rate upon the adsorbate concentration observed 407 experimentally (Figure 2c) is then defined within the rate equation, giving:

$$\frac{dq_t}{dt} = k'C_t \left(1 - \frac{q_t}{q_e}\right)^2$$

Equation 11

Equation 10

408

409 where
$$k' = \frac{k_2 q_e^2}{C_0}$$
. 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 C_s (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 C_s, due to its second-order dependence upon the absolute adsorption capacity remaining $(q_e-q_t)^2$ and the decrease in q_e with increasing C_s. In contrast, since the rPSO depends on the relative adsorption capacity remaining through the term $(1 - \frac{q_t}{q_e})^2$, this rate equation displays the zero-order dependency of C_s identified from analysis of the literature. The rPSO rate constant k' is therefore theoretically independent of changes in C_s, unlike the original PSO rate constant k₂. The

- 417 rPSO model is similar to the adsorption-only form of the kinetic Langmuir model (kLm), which at high 418 surface coverage is first order with respect to C_t and second order to $(1 - \frac{q_t}{q_c})^{37}$.
- 419

420 Validation of the rPSO rate equation

The removal of experimental conditionality (i.e. the dependency upon C₀ and C_s) from the revised 421 422 model was verified using experimental data from the literature. The ideal rate constant is unaffected 423 by the experimental conditions, and subsequently the dependency of the rate constant with respect 424 to C₀ and C_s should be zero. These dependencies were calculated from the slope of log(rate 425 constant) versus $log(C_0)$ or $log(C_s)$. As highlighted by Figure 4a, the original PSO rate constant k_2 is 426 strongly dependent upon the experimental conditions, being inversely proportional to C₀ and 427 second-order with respect to C_s. The average C₀ dependency is -0.73±0.46, and the average C_s 428 dependency is 1.57±0.79. In contrast, k' is approximately zero-order with respect to both 429 experimental variables. Furthermore, the dependencies of k' upon C_0 and C_s vary less (there is less 430 scattering) than k_2 . The average C_0 dependency is -0.20±0.38 and the average C_s dependency is 431 0.10 \pm 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 C_s is captured by the new model. 432

When the adsorbate is in excess ($q_e < C_0$) the rPSO model approximates the form of the original PSO 433 434 model. At higher values of q_e relative to C₀, the graphical form of the two models deviates, due to 435 the rPSO kinetics decreasing more rapidly than PSO kinetics due to the consumption of the 436 adsorption, which decreases the parameter Ct. (However, this effect is logical, given that at low Ct 437 values, the rate of adsorption will be limited by the availability of adsorbate). Therefore, rate 438 constants for the rPSO (k') can be readily calculated from PSO parameters k_2 and q_e when the adsorbate is in excess, using the formula $k' = \frac{k_2 q_e^2}{C_0}$. When the adsorbent removes the majority of 439 440 the adsorbate, however, the rPSO model will require re-fitting due to the increasing difference in the graphical form of the PSO and rPSO models. 441



443 Figure 4: Verifying that experimental conditionality (with respect to C_0 and C_2) is decreased in the rPSO model versus the 444 original PSO model. (a) The dependencies of the original PSO rate constant k_2 and the rPSO rate constant k' upon C_0 and C_5 445 were calculated from the slope of log plots, as per Figure 3, with the ideal rate constant giving a reaction order or 446 'dependency' of zero. The data is shown as normal distributions with the mean and standard deviation set equal to the 447 slope and standard error of the slope in the log plots (with 9 data sets for C_0 and 8 for C_s). These values are: -0.73±0.46 for k_2 and C_0 ; 1.57±0.79 for k_2 and C_s ; -0.20±0.38 for k' and C_0 ; 0.10±0.45 for k' and C_s . (b) A comparison of the form of the 448 original PSO equation with the rPSO equation, with different $\frac{C_0}{q_e}$ ratios (with $C_s=1$ g L^{-1}). The original PSO model is presented 449 in blue and the rPSO model in red, with $\frac{c_0}{a_2}$ equal to 1 (dotted lines), 2 (dashed lines), and 5 (solid lines). 450

452 **Example applications**

453

454

Application 1: Evaluating the predictive capability of 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 C_s.

The original PSO model tends to systematically overestimate q_t for experiments with high C_0 or low C_s values and systematically underestimate q_t for experiments with low C_0 or high C_s values (Figure 5). This is due to the negative and positive relationships between k_2 and C_0 and C_s respectively as previously discussed, with this relationship being denied when a single value of k_2 is used to model all experiments. The rPSO model gave 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) and the median decrease in the sum of squared residuals when changing from the PSO to the rPSO model was 66%.















(d)



(f)



Figure 5: Application study 1: Application of 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 C_0 is varied, and (d,e,f) present 3 experiments where C_s is varied. Experimental data was sourced 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.

475

The average relative error of q_t calculated by the rPSO is just 1±17%, versus -11±27% for the original 476 477 PSO model (Figure 6a), indicating that the rPSO model provides greater accuracy when modelling 478 adsorption kinetics with changing values of C₀ and C_s using a single rate constant. Furthermore, the 479 calibration curve of qt (model) against qt (experiment) is closer to the ideal one-to-one line in the 480 rPSO model, with an R² value of 0.999 versus just 0.9217 for the original PSO model (Figure 6b). 481 Considering each experimental data series in turn, the typical slope of the calibration curve was 482 closer to one, with less scattering, in the rPSO model (a slope of 0.99±0.11) compared against the 483 original PSO model (with a slope of 1.23±0.35) (Figure 6c).



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 q_t calculated via the original PSO model and the rPSO model. The boxes highlight the 25%, 50% (median) and 75% percentiles, whilst the whiskers represent

Bullen et al. (2021)

487 the minima and maxima excluding 'outlier' data points, defined as those greater than the top of the box plus 1.5 times the 488 interquartile range, or less than the bottom of the box minus 1.5 times the interquartile range. (b) Cross-calibration plot 489 highlighting the goodness of fit against the one-to-one line. Open shapes indicate q_t values calculated using the original PSO 490 model, whilst filled shapes indicate the rPSO model. Values of R^2 indicate the goodness of fit against the ideal one-to-one 491 line. (c) Comparison of the cross-calibration slopes with each model and each data set. Literature sources are denoted as (dark blue squares), As(V)/Fe₂O₃⁴¹ (light blue circles), HPO₄²⁻/iron hydroxide ⁴² (dark green diamonds), 492 As(III)/HFO 40 $Cr(VI)/Fe_2O_3^{43}$ (light green triangles), Cr(VI)/Mg-Al-CO₃⁴⁴ (orange squares), and $Cd(II)/Fe_2O_3^{45}$ (red circles). Further results 493 494 are presented in SI Figure S3.

495

496 Whilst the rPSO rate constant k' appears to be more stable to changes in experimental conditions 497 than the PSO rate constant k_2 , the parameter q_e is conditional, depending upon C_0 and C_s . For 498 predictive modelling, this limitation can be rectified by using an adsorption isotherm to predict q_e (such as the Langmuir or Freundlich model 46). Though a single value of q_e can be determined for the 499 entirety of each experiment, in scenarios such as a column reactor the equilibrium adsorbate 500 501 concentration parameter C_e has diminished physical significance, and it may be better to replace this 502 term with C_t , recalculating the hypothetical value of q_e at each point in time. Huang et al. previously 503 demonstrated that this approach can give a better account of the true driving force of the reaction

504 during the initial stages of adsorption ⁴⁷.

505

506

Application 2: Comparison of rate constants between different experimental studies

507 Comparison of the rPSO rate constant k' is expected to be more meaningful and more appropriate 508 than k_2 when comparing the adsorption kinetics reported in the literature using different 509 experimental conditions, since some of the experimental conditionality (towards changes in C₀ and 510 C_s) is accounted for. To demonstrate the potential application of normalised rate constants towards 511 achieving a meaningful comparison of the adsorption kinetics reported across the literature, we 512 collected 14 and 7 literature sources reporting the kinetics of inorganic arsenic As(V) and As(III) 513 adsorption onto iron oxide and alumina adsorbents respectively.

The average value of $log(k_2)$ 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 large, with more than an order of magnitude variation in k_2 and k' values: neither model provides a rate constant that is generally valid for iron oxide adsorbents used by different studies. Similarly, the adsorption of inorganic arsenic onto alumina gives average values of $log(k_2) = 0.98\pm1.84$ and $log(k') = 0.35\pm1.75$.

519 Whilst the variation in both k_2 and k' across the literature is large, the influence of adsorbent 520 morphology on adsorption kinetics has not been incorporated into either of the PSO and rPSO 521 models. Adsorption kinetics are often faster for adsorbent materials with smaller particles, due to 522 the improved rate of mass transport of the adsorbate to adsorbent surface sites ⁴⁸. For instance, in 523 intraparticle diffusion model gives a rate of adsorption that is proportional to r⁻¹ (where r is particle 524 size) ⁴⁹.

525 Whilst a faster reaction is anticipated for small iron oxide particle sizes, plotting $log(k_2)$ as a function 526 of $log(r^{-1})$ shows a weak inverse relationship (linear regression gives a slope of -0.49±0.20 and 527 R²=0.3234) (Figure 7a). This is due to the significant increase in q_e as the particle size decreases (SI 528 Figure S4) and the inverse relationship between k_2 and q_e through the term $(q_e-q_t)^2$ as previously 529 discussed. In contrast, alumina shows the anticipated positive relationship (with a slope of 0.61 ± 0.28 530 and R²=0.4783). Since adsorption onto smaller particles is typically faster than onto larger particles,

531 the comparison of k₂ values for different adsorbent sizes and different adsorbent materials (i.e. iron

532 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 533 534 iron oxide and alumina adsorbents (Figure 7b). For the iron oxides we see a slope of 0.44±0.1 with 535 R²=0.5211, and for alumina we see a slope of 0.62±0.25 and R²=0.5547. The limited goodness of fit in 536 the linear regression is controlled by factors including poor characterisation of the particle size and differences in experimental conditions beyond C₀ and C_s, such as the pH. The accurate 537 characterisation of particle size is especially challenging, given the range of techniques used by the 538 539 literature including transmission electron microscopy (TEM), dynamic light scattering (DLS) and sieve 540 fractionation.

541 The results from this literature survey show greater values of log(k') at each specific particle size for 542 alumina versus iron oxides, suggesting that the adsorption of inorganic arsenic is faster onto alumina 543 than onto iron oxides. With more rigorous analysis, such a study would have important implications 544 in the design of engineered solutions for arsenic remediation, i.e. opting to use alumina in place of 545 iron oxides when high flow rates in a column filter are required, or when larger particle sizes are 546 necessary to achieve the desired flow rate and porosity. This highlights that normalisation of the PSO 547 rate constant k_2 to the rPSO rate constant k', or some other constant, can achieve a more 548 meaningful comparison of the adsorption kinetics reported by the literature.





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.

555 **Conclusions**

556

557 This work aimed to modify the popular pseudo-second order (PSO) model of adsorption kinetics to 558 remove experimental conditionality, focusing upon initial adsorbate concentration (C_0) and adsorbent concentration (C_s). A revised PSO rate equation (rPSO) was developed from the empirical 559 analysis of 69 kinetic experiments taken from 15 literature sources. The final equation takes the 560 form $\frac{dq_t}{dt} = k'C_t(1-\frac{q_t}{q_e})^2$. The first application study demonstrates that the rPSO equation allows 561 562 for a single rate constant to model multiple experiments, differing in the experimental conditions C₀ and C_s, with greater accuracy and a 66% decrease in the sum of squared residuals versus the original 563 564 PSO model. The second application study demonstrates that the rPSO equation provides a rate 565 constant which is more useful for comparison across the literature than the PSO rate constant k_2 , obeying the anticipated relationship between adsorption rates and particle size. 566

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 C_t and second order with respect to $(1 - \frac{q_t}{q_e})^{37 38}$. 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

571 PSO model in engineering studies where operating conditions are likely to vary.

- 572 One of the reasons for the popularity of the original PSO model is its linearised forms, from which k_2 573 and q_e 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.
- 576 Where necessary, the rate constant for this revised model can be quickly obtained from linearised
- $^{+2}$

577 PSO kinetics using the expression $k' = \frac{k_2 q_e^{+2}}{c_0^{+}}$.

- 578 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 C_0 was varied and 8 where C_s was varied, satisfying our requirements for early kinetic data
- with $\frac{q_t}{q_e} < 0.6$. This highlights a need for experimental work to investigate the influence of these
- ^{qe}
 583 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 .
- 586
- 587

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592 Supporting information

593 The supplementary information provides references to all data sets used in this work; figures 594 showing the influence of adsorbent morphology on k_2 ; and tabulates all parameters (q_e , k_2 , k' and 595 initial rate) calculated in this work.

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