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

Supplementary Information

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# Data sets

Table S: Data sets collected, and the experimental conditions varied across each data set. C0 is the initial adsorbate concentration (mg L-1), Cs is the adsorbent concentration (g L-1) and r is particle radius (nm, μm or mm).

| Sorbate | Sorbent | Which experiments was the data used for? | Reference | |
| --- | --- | --- | --- | --- |
| Cd(II) | graphene oxide-Fe3O4-C3N3S3 | Influence of early data availability on the calculation of initial rates | 1 | |
| Reactive yellow | Activated carbon | Initial rates | 2 | |
| Antibiotics | Activated carbon | Initial rates | 3 | |
| Methylene blue | Polymer-grafted magnetic microspheres | Initial rates | 4 | |
| Pyridine | Polystyrene | Initial rates | 5 | |
| Congo red | Shiitake mushroom | Initial rates | 6 | |
| As(V) | Lanthanum-modified ceramics | Initial rates | 7 | |
| Pb(II) | Algae biomass | Initial rates | 8 | |
| PO43- | Fe3O4-SiO2 | Initial rates | 9 | |
| Cr(III) | Kaolin | Initial rates | 10 | |
| Pb(II) | Sulphuric acid treated acorn waste | Initial rates | 11 | |
| Zn(II) | Regenerated cellulose | Initial rates | 12 | |
| Tetracycline | Biochar | Initial rates | 13 | |
| Methyl orange | Coal-kaolinite composite | Initial rates | 14 | |
| As(V) | Fe2O3 | Initial adsorbate concentration, C0 | 15 | |
| As(V) | Laterite | C0 | 16 | |
| As(III) | Hydrous ferric oxide | C0 | 17 | |
| HPO42- | Iron hydroxide | C0 | 18 | |
| Cr(VI) | Activated carbon | C0 | 19 | |
| Cu(II) | Soil | C0 | 20 | |
| Pb(II) | Soil | C0 | 20 | |
| Hg(II) | Raw activated sludge | C0 | 21 | |
| Rose Bengal dye | ZnCl2-activated carbon | C0 | 22 | |
| Cr(VI) | Fe2O3 | Adsorbent concentration, Cs | 23 | |
| Cr(VI) | Mg-Al-CO3 | Cs | 24 | |
| Cr(VI) | Chitin | Cs | 25 | |
| Cu(II) | Fe2O3 | Cs | 26 | |
| Zn(II) | Fe2O3 | Cs | 26 | |
| Hg(II) | Lessonia nigrescens (kelp) | Cs | 27 | |
| Hg(II) | Lessonia trabeculata (kelp) | Cs | 27 | |
| Methylene blue | Raffia fibres | Cs | 28 | |
| As(V) | Fe2O3 | particle size, r | 15 |
| As(V) | Fe2O3 | r | 29 |
| As(V) | Fe2O3 | r | 30 |
| As(V) | Fe2O3 | r | 31 |
| As(V) | Fe2O3 | r | 32 |
| As(V) | Fe2O3 | r | 33 |
| As(V) | Fe3O4 | r | 31 |
| As(V) | Fe3O4 | r | 34 |
| As(V) | Fe3O4 | r | 35 |
| As(V) | Fe3O4 | r | 36 |
| As(V) | Fe3O4 | r | 37 |
| As(V) | Fe3O4 | r | 34 |
| As(V) | FeOOH | r | 38 |
| As(V) | FeOOH | r | 31 |
| As(V) | FeOOH | r | 39 |
| As(V) | FeOOH | r | 40 |
| As(V) | FeOOH | r | 41 |
| As(III) | Fe2O3 | r | 30 |
| As(III) | Fe2O3 | r | 31 |
| As(III) | Fe2O3 | r | 32 |
| As(III) | Fe2O3 | r | 33 |
| As(III) | Fe3O4 | r | 31 |
| As(III) | Fe3O4 | r | 34 |
| As(III) | Fe3O4 | r | 36 |
| As(V) | Al2O3 | r | 42 |
| As(V) | Al2O3 | r | 43 |
| As(V) | Al2O3 | r | 44 |
| As(V) | Al2O3 | r | 45 |
| As(III) | Al2O3 | r | 46 |
| As(III) | Al2O3 | r | 42 |
| As(III) | Al2O3 | r | 45 |

# Comparison of mathematical techniques for the calculation of initial rates

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Figure S: The influence of the availability of early kinetic data on the calculation of initial rates using three mathematical approaches. Experiments from the literature were analysed (N=14), recalculating the initial rate as early data was consecutively removed, using three approaches: the initial slope approach (open diamonds), linearised PSO kinetics (red squares) and non-linear PSO kinetics (blue circles).

# Determining the order of reaction

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

Figure S: Legend for the different adsorbate-adsorbent combinations presented in (a) Figure 2a and 3a, and (b) Figure 2b and 3b of the main text respectively.

# Application study 1

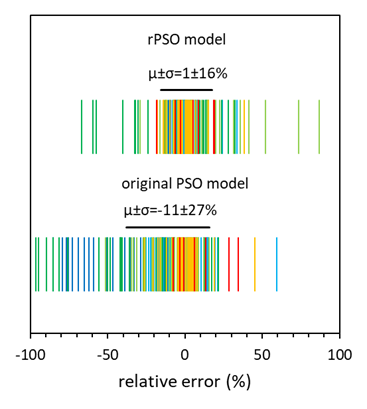


Figure S: Application study 1: Stick plot highlighting the relative error of qt calculated via the original PSO model and the rPSO (6 literature sources, 22 experiments and 198 data points). The average value and its standard deviation is indicated by μ±σ. Literature sources are denoted as As(III)/HFO 17 (dark blue squares), As(V)/Fe2O3 15 (light blue circles), HPO42-/iron hydroxide 18 (dark green diamonds), Cr(VI)/Fe2O3 23 (light green triangles), Cr(VI)/Mg-Al-CO3 24 (orange squares), and Cd(II)/Fe2O3 26 (red circles).

# Application study 2

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

Figure S: (a) The influence of particle radius (r) on the equilibrium adsorption capacity (qe) for the adsorption of inorganic As(V) and As(III) onto iron oxide adsorbents (red and orange filled shapes respectively) and inorganic As(V) and As(III) onto alumina adsorbents (dark blue open squares and light blue open circles respectively). Values of qe were determined by fitting the original PSO kinetic model. (b) Values of initial adsorbate concentration (C0) for the same experiments.

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Figure S: Legend indicating the different adsorbate-adsorbent systems presented in Application study 2.

# References

(1) Yang, H.; Yu, H.; Fang, J.; Sun, J.; Xia, J.; Xie, W.; Wei, S.; Cui, Q.; Sun, C.; Wu, T. Mesoporous Layered Graphene Oxide/Fe3O4/C3N3S3 Polymer Hybrids for Rapid Removal of Pb2+ and Cd2+ from Water. *ACS Omega* **2019**, *4* (22), 19683–19692. https://doi.org/10.1021/acsomega.9b02347.

(2) Yang, X. Y.; Al-Duri, B. Application of Branched Pore Diffusion Model in the Adsorption of Reactive Dyes on Activated Carbon. *Chem. Eng. J.* **2001**, *83* (1), 15–23. https://doi.org/10.1016/S1385-8947(00)00233-3.

(3) Liu, Y.; Shen, L. From Langmuir Kinetics to First- and Second-Order Rate Equations for Adsorption. *Langmuir* **2008**, *24* (20), 11625–11630. https://doi.org/10.1021/la801839b.

(4) Xu, B.; Zheng, C.; Zheng, H.; Wang, Y.; Zhao, C.; Zhao, C.; Zhang, S. Polymer-Grafted Magnetic Microspheres for Enhanced Removal of Methylene Blue from Aqueous Solutions. *RSC Adv.* **2017**, *7* (74), 47029–47037. https://doi.org/10.1039/c7ra06810g.

(5) Zhu, Q.; Moggridge, G. D.; D’Agostino, C. Adsorption of Pyridine from Aqueous Solutions by Polymeric Adsorbents MN 200 and MN 500. Part 2: Kinetics and Diffusion Analysis. *Chem. Eng. J.* **2016**, *306*, 1223–1233. https://doi.org/10.1016/j.cej.2016.07.087.

(6) Yang, K.; Li, Y.; Zheng, H.; Luan, X.; Li, H.; Wang, Y.; Du, Q.; Sui, K.; Li, H.; Xia, Y. Adsorption of Congo Red with Hydrothermal Treated Shiitake Mushroom. *Mater. Res. Express* **2019**, *7* (1). https://doi.org/10.1088/2053-1591/ab5ff3.

(7) Yang, H.; Wang, Y.; Bender, J.; Xu, S. Removal of Arsenate and Chromate by Lanthanum-Modified Granular Ceramic Material: The Critical Role of Coating Temperature. *Sci. Rep.* **2019**, *9* (1), 1–12. https://doi.org/10.1038/s41598-019-44165-8.

(8) Mohamed, S. F.; Al-Bakri, I. M.; El Sayed, O. H. Biosorption of Lead (II) by Pre-Treated Biomass of Marine Brown Algae Sargassum Latifolium and Sargassum Asperifolium. *Biosci. Biotechnol. Res. Asia* **2007**, *4* (2), 341–350.

(9) Drenkova-tuhtan, A.; Mandel, K.; Meyer, C.; Schneider, M. Removal and Recovery of Phosphate from Wastewater with Reusable Magnetically Separable Particles. *IWA Spec. Conf. Nutr. Remov. Recover. Mov. Innov. into Pract.* **2015**, No. May. https://doi.org/10.13140/RG.2.1.1260.8721.

(10) Liu, J.; Wu, X.; Hu, Y.; Dai, C.; Peng, Q.; Liang, D. Effects of Cu(II) on the Adsorption Behaviors of Cr(III) and Cr(VI) onto Kaolin. *J. Chem.* **2016**, *2016* (Vi). https://doi.org/10.1155/2016/3069754.

(11) Örnek, A.; Özacar, M.; Şengil, I. A. Adsorption of Lead onto Formaldehyde or Sulphuric Acid Treated Acorn Waste: Equilibrium and Kinetic Studies. *Biochem. Eng. J.* **2007**, *37* (2), 192–200. https://doi.org/10.1016/j.bej.2007.04.011.

(12) Zhan, W.; Xu, C.; Qian, G.; Huang, G.; Tang, X.; Lin, B. Adsorption of Cu(Ii), Zn(Ii), and Pb(Ii) from Aqueous Single and Binary Metal Solutions by Regenerated Cellulose and Sodium Alginate Chemically Modified with Polyethyleneimine. *RSC Adv.* **2018**, *8* (33), 18723–18733. https://doi.org/10.1039/c8ra02055h.

(13) Ai, T.; Jiang, X.; Liu, Q.; Lv, L.; Dai, S. Single-Component and Competitive Adsorption of Tetracycline and Zn(Ii) on an NH4Cl-Induced Magnetic Ultra-Fine Buckwheat Peel Powder Biochar from Water: Studies on the Kinetics, Isotherms, and Mechanism. *RSC Adv.* **2020**, *10* (35), 20427–20437. https://doi.org/10.1039/d0ra02346a.

(14) Nadiye-tabbiruka, M. S.; Sejie, F. P. Preparation of Coal-Kaolinite Nano Composites and Investigation of Their Use to Remove Methyl Orange from Water. **2019**, *9* (2), 37–43. https://doi.org/10.5923/j.nn.20190902.01.

(15) Singh, D. B.; Prasad, G.; Rupainwar, D. C. Adsorption Technique for the Treatment of As(V)-Rich Effluents. *Colloids Surfaces A Physicochem. Eng. Asp.* **1996**, *111* (1–2), 49–56. https://doi.org/10.1016/0927-7757(95)03468-4.

(16) Maiti, A.; Basu, J. K.; De, S. Desorption Kinetics and Leaching Study of Arsenic from Arsenite/Arsenate-Loaded Natural Laterite. *Int. J. Environ. Technol. Manag.* **2010**, *12* (2/3/4), 294. https://doi.org/10.1504/ijetm.2010.031534.

(17) Manna, B. R.; Dey, S.; Debnath, S.; Ghosh, U. C. Removal of Arsenic from Groundwater Using Crystalline Hydrous Ferric Oxide (CHFO). *Water Qual. Res. J. Canada* **2003**, *38* (1), 193–210. https://doi.org/10.2166/wqrj.2003.013.

(18) Mezenner, N. Y.; Bensmaili, A. Kinetics and Thermodynamic Study of Phosphate Adsorption on Iron Hydroxide-Eggshell Waste. *Chem. Eng. J.* **2009**, *147* (2–3), 87–96. https://doi.org/10.1016/j.cej.2008.06.024.

(19) Aworanti, A.; Agarry, S. E. Kinetics, Isothermal and Thermodynamic Modelling Studies of Hexavalent Chromium Ions Adsorption from Simulated Wastewater onto Parkia Biglobosa -Sawdust Derived Acid-Steam Activated. *Appl. J. Environ. Eng. Sci.* **2017**, *3* (1), 58–76.

(20) Lim, S. F.; Lee, A. Y. W. Kinetic Study on Removal of Heavy Metal Ions from Aqueous Solution by Using Soil. *Environ. Sci. Pollut. Res.* **2015**, *22* (13), 10144–10158. https://doi.org/10.1007/s11356-015-4203-6.

(21) Natarajan, R.; Manivasagan, R. Biosorptive Removal of Heavy Metal onto Raw Activated Sludge: Parametric, Equilibrium, and Kinetic Studies. *J. Environ. Eng. (United States)* **2016**, *142* (9). https://doi.org/10.1061/(ASCE)EE.1943-7870.0000961.

(22) Nandhakumar, V. Adsorption of Rose Bengal Dye from Aqueous Solution onto Zinc Chloride Activated Carbon. *SOJ Mater. Sci. Eng.* **2015**, *3* (2), 1–9. https://doi.org/10.15226/sojmse.2015.00126.

(23) Debnath, A.; Bera, A.; Chattopadhyay, K. K.; Saha, B. Facile Additive-Free Synthesis of Hematite Nanoparticles for Enhanced Adsorption of Hexavalent Chromium from Aqueous Media: Kinetic, Isotherm, and Thermodynamic Study. *Inorg. Nano-Metal Chem.* **2017**, *47* (12), 1605–1613. https://doi.org/10.1080/24701556.2017.1357581.

(24) Lazaridis, N. K.; Pandi, T. A.; Matis, K. A. Chromium(VI) Removal from Aqueous Solutions by Mg-Al-CO3 Hydrotalcite: Sorption-Desorption Kinetic and Equilibrium Studies. *Ind. Eng. Chem. Res.* **2004**, *43* (9), 2209–2215. https://doi.org/10.1021/ie030735n.

(25) Saǧ, Y.; Aktay, Y. Mass Transfer and Equilibrium Studies for the Sorption of Chromium Ions onto Chitin. *Process Biochem.* **2000**, *36* (1–2), 157–173. https://doi.org/10.1016/S0032-9592(00)00200-4.

(26) Shipley, H. J.; Engates, K. E.; Grover, V. A. Removal of Pb(II), Cd(II), Cu(II), and Zn(II) by Hematite Nanoparticles: Effect of Sorbent Concentration, PH, Temperature, and Exhaustion. *Environ. Sci. Pollut. Res.* **2013**, *20* (3), 1727–1736. https://doi.org/10.1007/s11356-012-0984-z.

(27) Reategui, M.; Maldonado, H.; Ly, M.; Guibal, E. Mercury(II) Biosorption Using Lessonia Sp. Kelp. *Appl. Biochem. Biotechnol.* **2010**, *162* (3), 805–822. https://doi.org/10.1007/s12010-010-8912-5.

(28) Staroń, P.; Chwastowski, J.; Banach, M. Sorption Behavior of Methylene Blue from Aqueous Solution by Raphia Fibers. *Int. J. Environ. Sci. Technol.* **2019**, *16* (12), 8449–8460. https://doi.org/10.1007/s13762-019-02446-9.

(29) Arai, Y.; Sparks, D. L.; Davis, J. A. Effects of Dissolved Carbonate on Arsenate Adsorption and Surface Speciation at the Hematite-Water Interface. *Environ. Sci. Technol.* **2004**, *38* (3), 817–824. https://doi.org/10.1021/es034800w.

(30) Dickson, D.; Liu, G.; Cai, Y. Adsorption Kinetics and Isotherms of Arsenite and Arsenate on Hematite Nanoparticles and Aggregates. *J. Environ. Manage.* **2017**, *186*, 261–267. https://doi.org/10.1016/j.jenvman.2016.07.068.

(31) Giménez, J.; Martínez, M.; de Pablo, J.; Rovira, M.; Duro, L. Arsenic Sorption onto Natural Hematite, Magnetite, and Goethite. *J. Hazard. Mater.* **2007**, *141* (3), 575–580. https://doi.org/10.1016/j.jhazmat.2006.07.020.

(32) Tang, W.; Li, Q.; Gao, S.; Shang, J. K. Arsenic (III,V) Removal from Aqueous Solution by Ultrafine α-Fe2O3 Nanoparticles Synthesized from Solvent Thermal Method. *J. Hazard. Mater.* **2011**, *192* (1), 131–138. https://doi.org/10.1016/j.jhazmat.2011.04.111.

(33) Cheng, W.; Zhang, W.; Hu, L.; Ding, W.; Wu, F.; Li, J. Etching Synthesis of Iron Oxide Nanoparticles for Adsorption of Arsenic from Water. *RSC Adv.* **2016**, *6* (19), 15900–15910. https://doi.org/10.1039/c5ra26143k.

(34) Monárrez-Cordero, B. E.; Amézaga-Madrid, P.; Leyva-Porras, C. C.; Pizá-Ruiz, P.; Miki-Yoshida, M. Study of the Adsorption of Arsenic (III and V) by Magnetite Nanoparticles Synthetized via AACVD. *Mater. Res.* **2016**, *19*, 103–112. https://doi.org/10.1590/1980-5373-MR-2015-0667.

(35) Luo, H.; Cheng, F.; Hu, W.; Wang, J.; Xiang, S.; Fidalgo de Cortalezzi, M. 2D-Fe3O4 Nanosheets for Effective Arsenic Removal. *J. Contemp. Water Res. Educ.* **2017**, *160* (1), 132–143. https://doi.org/10.1111/j.1936-704x.2017.03245.x.

(36) Chowdhury, S. R.; Yanful, E. K. Arsenic and Chromium Removal by Mixed Magnetite-Maghemite Nanoparticles and the Effect of Phosphate on Removal. *J. Environ. Manage.* **2010**, *91* (11), 2238–2247. https://doi.org/10.1016/j.jenvman.2010.06.003.

(37) Baig, S. A.; Sheng, T.; Sun, C.; Xue, X.; Tan, L.; Xu, X. Arsenic Removal from Aqueous Solutions Using Fe3O4-HBC Composite: Effect of Calcination on Adsorbents Performance. *PLoS One* **2014**, *9* (6). https://doi.org/10.1371/journal.pone.0100704.

(38) Zhang, J.; Stanforth, R. Slow Adsorption Reaction between Arsenic Species and Goethite (α-FeOOH): Diffusion or Heterogeneous Surface Reaction Control. *Langmuir* **2005**, *21* (7), 2895–2901. https://doi.org/10.1021/la047636e.

(39) Wei, Y.; Wei, S.; Liu, C.; Chen, T.; Tang, Y.; Ma, J.; Yin, K.; Luo, S. Efficient Removal of Arsenic from Groundwater Using Iron Oxide Nanoneedle Array-Decorated Biochar Fibers with High Fe Utilization and Fast Adsorption Kinetics. *Water Res.* **2019**, *167*, 115107. https://doi.org/10.1016/j.watres.2019.115107.

(40) Simsek, E. B.; Beker, U. Kinetic Performance of Aluminum and Iron Oxides in the Removal of Arsenate from Aqueous Environment. *J. Clean Energy Technol.* **2014**, *2* (3), 206–209. https://doi.org/10.7763/jocet.2014.v2.124.

(41) Grafe, M.; Eick, M. J.; Grossl, P. R. Adsorption of Arsenate (V) and Arsenite (III) on Goethite in the Presence and Absence of Dissolved Organic Carbon. *Soil Sci. Soc. Am. J.* **2010**, *65* (6), 1680. https://doi.org/10.2136/sssaj2001.1680.

(42) Singh, T. S.; Pant, K. K. Kinetics and Mass Transfer Studies on the Adsorption of Arsenic onto Activated Alumina and Iron Oxide Impregnated Activated Alumina. *Water Qual. Res. J. Canada* **2006**, *41* (2), 147–156. https://doi.org/10.2166/wqrj.2006.017.

(43) Romero Toledo, R.; Ruiz Santoyo, V.; Anaya Esparza, L. M.; Pérez Larios, A.; Martínez Rosales, M. Study of Arsenic (V) Removal of Water by Using Agglomerated Alumina. *Nov. Sci.* **2019**, *11* (23), 01–25. https://doi.org/10.21640/ns.v11i23.1665.

(44) Jeong, Y. The Adsorption of Arsenic (V) by Iron (Fe2O3) and Aluminum (Al2O3) Oxides, Iowa State University, 2005.

(45) Ghosh, S.; Prabhakar, R.; Samadder, S. R. Performance of Γ-Aluminium Oxide Nanoparticles for Arsenic Removal from Groundwater. *Clean Technologies and Environmental Policy*. 2019, pp 121–138. https://doi.org/10.1007/s10098-018-1622-3.

(46) Lin, T.; Wu, J. Adsorption of Arsenite and Arsenate within Activated Alumina Grains: Equilibrium and Kinetics. *Water Res.* **2001**, *35* (8), 2049–2057.