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232.0

92
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238.0

Uptake Kinetics of Heavy Metals from Water using a High Surface Area Supported Inorganic Metal Oxide

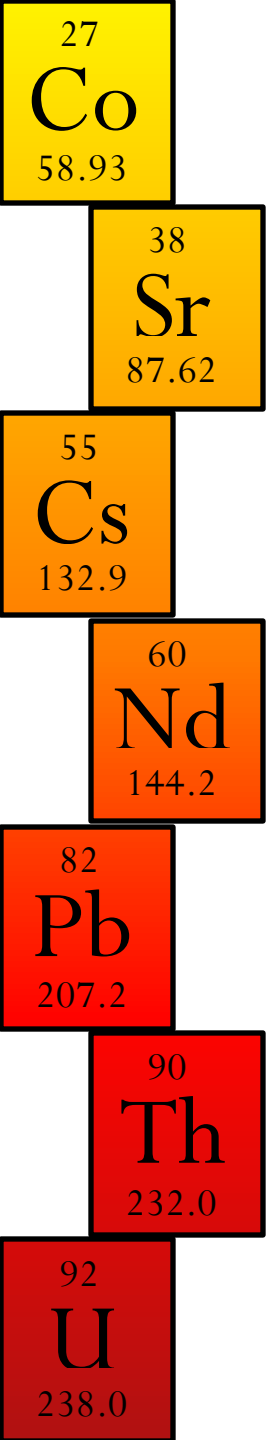
Wesley T. Honeycutt

Hayden Hamby

Allen Apblett

Nicholas F. Materer

April 12th, 2014



Overview

- Water remediation remains one of the most important environmental challenges.
- Straightforward extraction of heavy metal ions provides a manageable way to purify:
  - Mine Water
  - Water near anthropogenic radionuclides
    - Nuclear plant failure
    - Warzones
  - Poisoned aquifers

Babel, S. & Kurniawan, T. A. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* **97,** 219–243 (2003).

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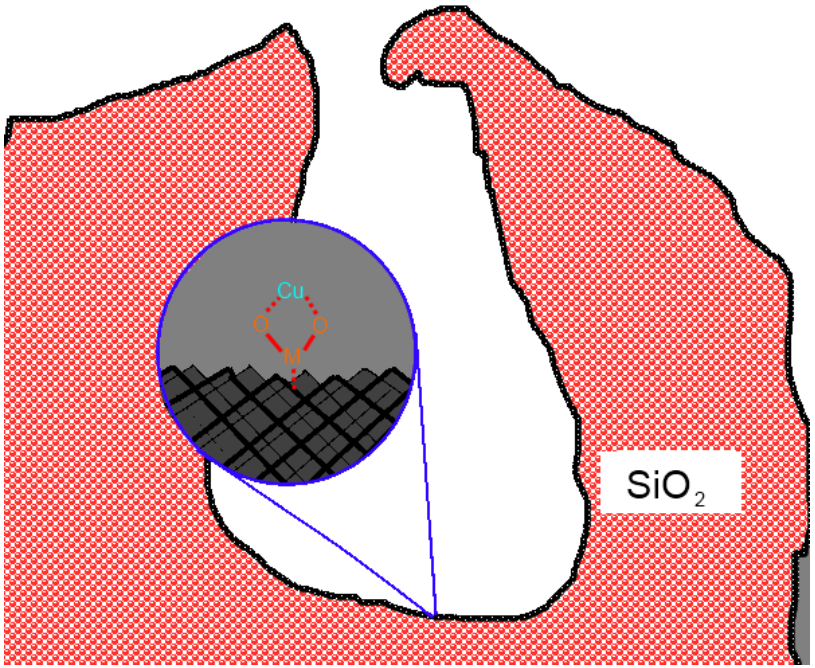
Metal Oxide

XMO_n

- Metal oxide bonded to high surface area silica.
- Selective for heavy ions with large radius.
- X leaves and is replaced by ion exchange pathway.



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Adsorption

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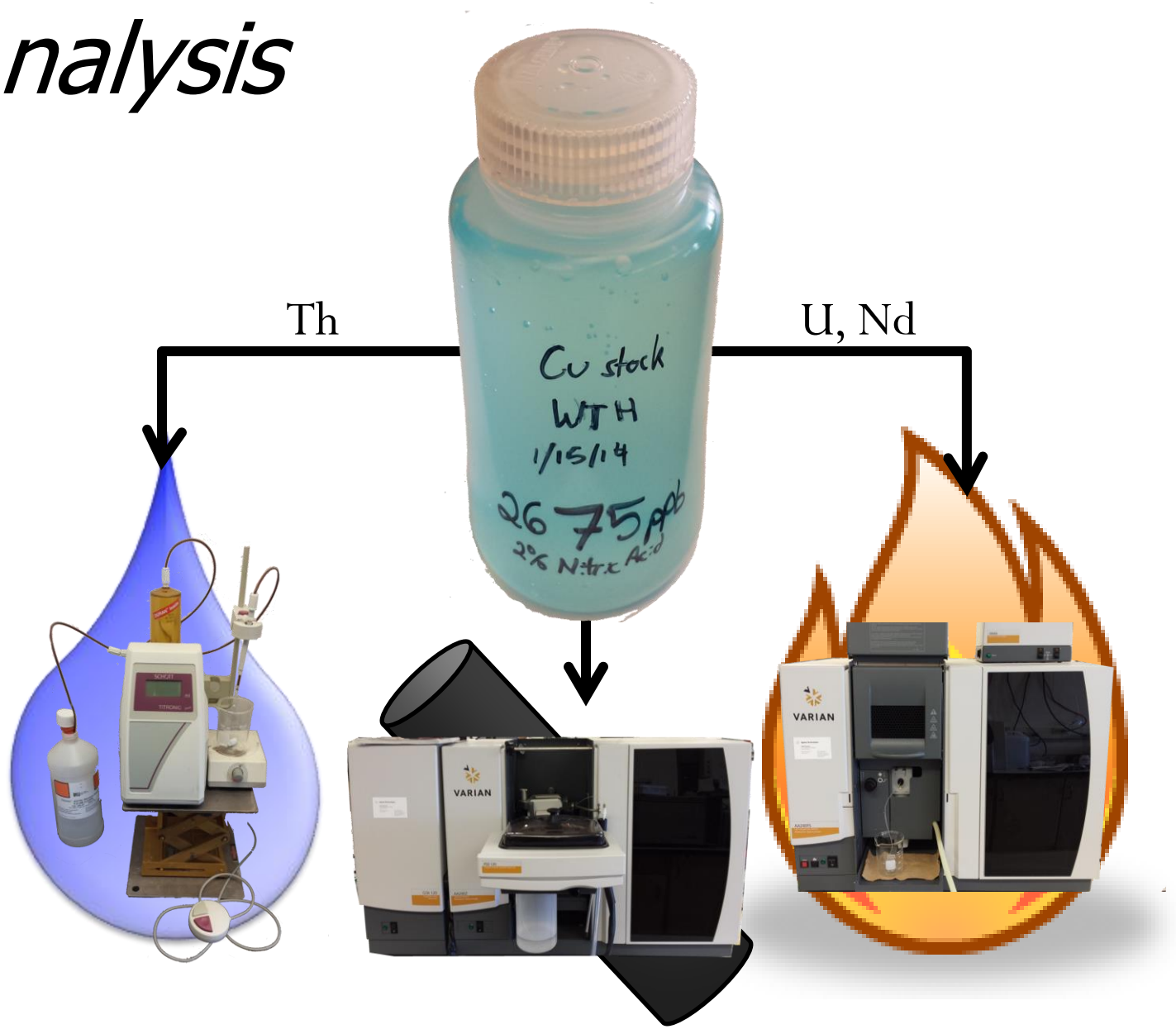
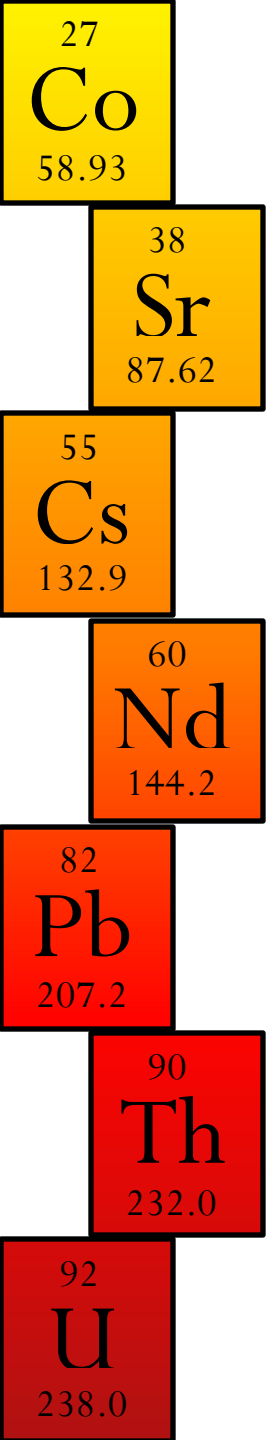
Analysis



Sen, A. B. & Chauhan, V. B. S. Estimation of thorium, zirconium, aluminium etc. with EDTA and back titration with ferric chloride solution using hydroxy naphthoic acids as indicators. *Fresenius' Zeitschrift für analytische Chemie* **195,** 255–256 (1963).



Data Analysis: Linearization

Linearized

- Advantages
  - Easy to interpret
- Disadvantages
  - Requires math trickery
  - Intrinsic deviation

Non-Linearized

- Advantages
  - Direct output
- Disadvantages
  - Difficult to interpret
  - Painful curve fitting

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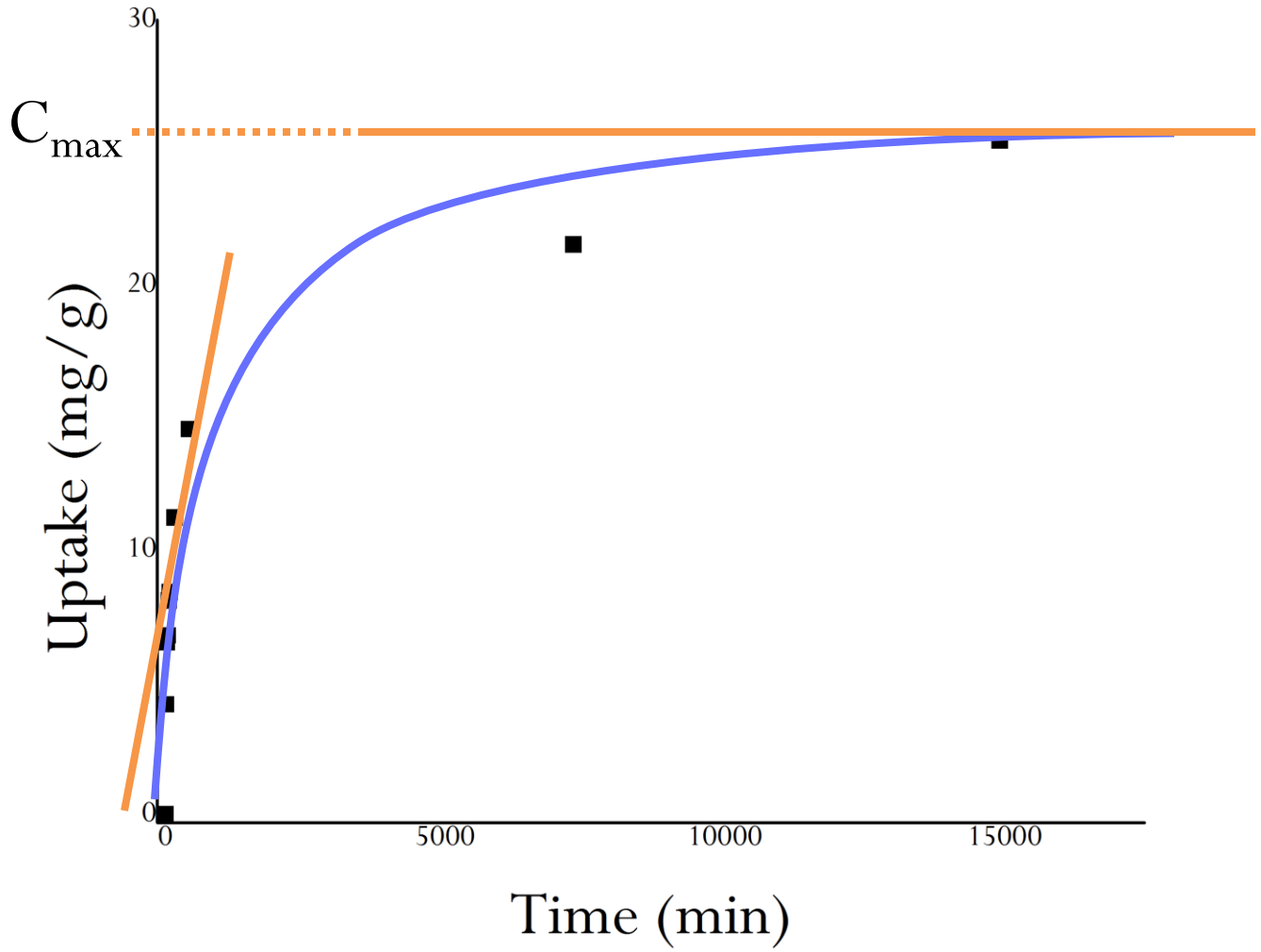
Concentration over Time: Generalized



Linearization of Simple Langmuir Isotherms

27 Co 58.93

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Eadie-Hofstee

$$q_t = q_e - \frac{1}{k}\left(\frac{q_t}{t}\right)$$

Scratchard

$$\frac{q_t}{t} = kq_e - kq_t$$

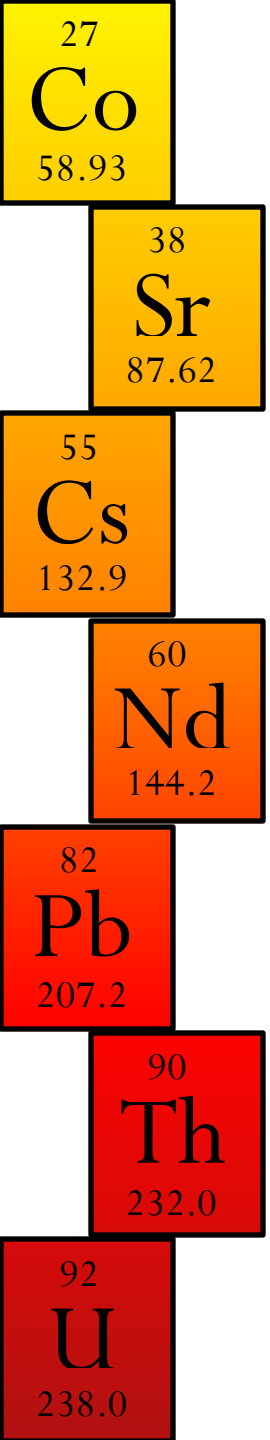
Hanes-Woolf

$$\frac{t}{q_t} = \frac{1}{q_e k} + \frac{t}{q_e}$$

Lineweaver-Burke

$$\frac{1}{q_t} = \frac{1}{kq_e}\left(\frac{1}{t}\right) + \frac{1}{q_e}$$

Bloster, C. H. & Hornberger, G. M. On the Use of Linearized Langmuir Equations. *Soil Sci. Soc. Am. J.* **71,** 1796–1806 (2007).



Linearized Langmuir Plots

	Residual ∑ Squares	Pearson's r	r^2
Eadie-Hofstee	1.0947	0.95959	0.91092
Scratchard	0.26964	0.95959	0.91092
Hanes-Woolf	11.589	0.86787	0.71794
Lineweaver-Burke	0.54053	-0.75803	0.51383

	Residual ∑ Squares	Pearson's r	r^2
Eadie-Hofstee	1.0947	0.95959	0.91092
Scratchard	0.26964	0.95959	0.91092
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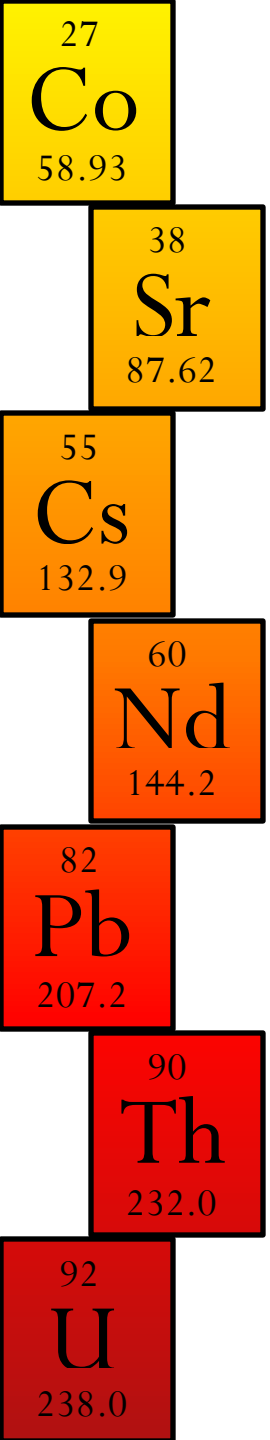

Pseudo-Order Kinetics

Pseudo-First Order

$$q_t = q_e(1 - e^{-k_1 t})$$

Pseudo-Second Order

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

Azizian, S. Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science* **276,** 47–52 (2004).
Ho, Y. . & McKay, G. Pseudo-second order model for sorption processes. *Process Biochemistry* **34,** 451–465 (1999).
Ho, Y.-S. Review of second-order models for adsorption systems. *Journal of Hazardous Materials* **136,** 681–689 (2006).
Lagergren, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe. Bihang Till K. Svenska Vet.-Akad. Handlingar **24** (1898).

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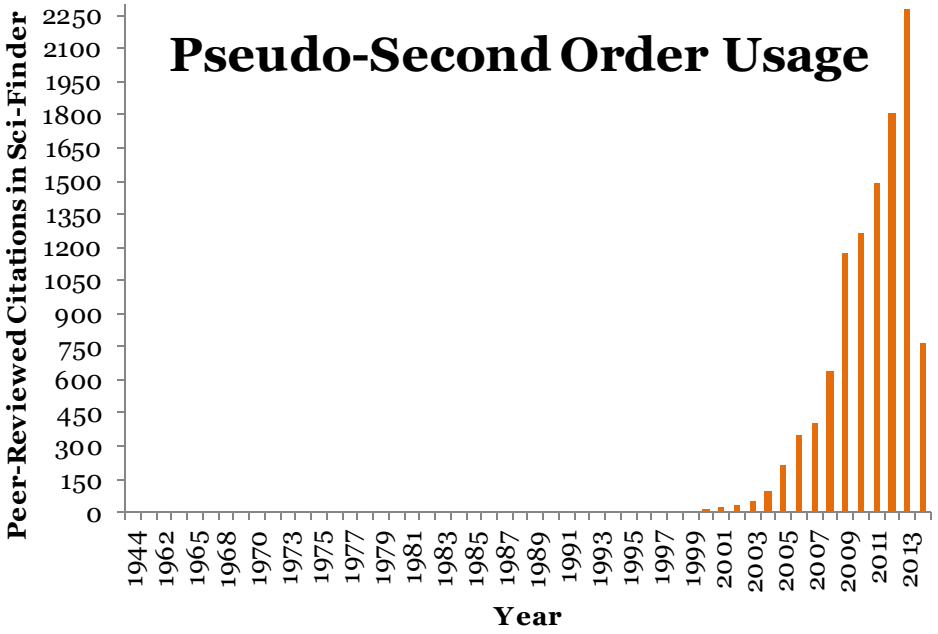
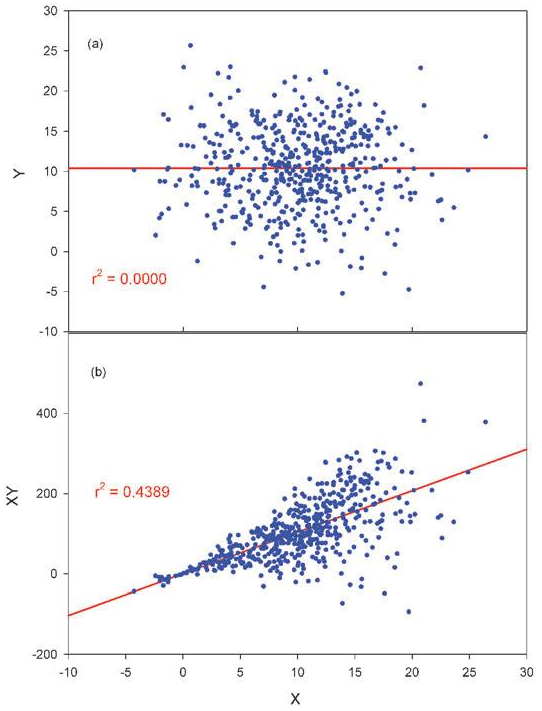
92 U 238.0

Pseudo-Second Order: Comments

0 of 2 Research Topic Candidates Selected — **References**

10700 references were found containing **"pseudo-second order"** as entered.	10700
16156 references were found containing the concept **"pseudo second order"**.	16156





Canzano, S., Iovino, P., Leone, V., Salvestrini, S. & Capasso, S. Use and Misuse of Sorption Kinetic Data: A Common Mistake that Should be Avoided. *Adsorption Science & Technology* **30,** 217–225 (2012).

Zhang, J.-Z. Avoiding spurious correlation in analysis of chemical kinetic data. *Chem. Commun.* **47,** 6861–6863 (2011).

"Pseudo-Second Order" Scifinder. ACS. Accessed Apr. 4th, 2014.

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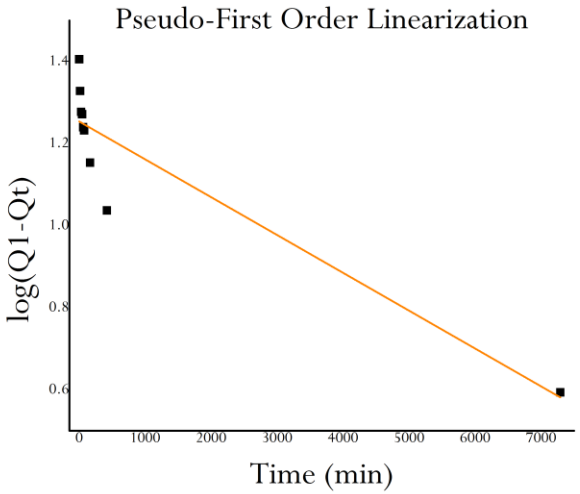
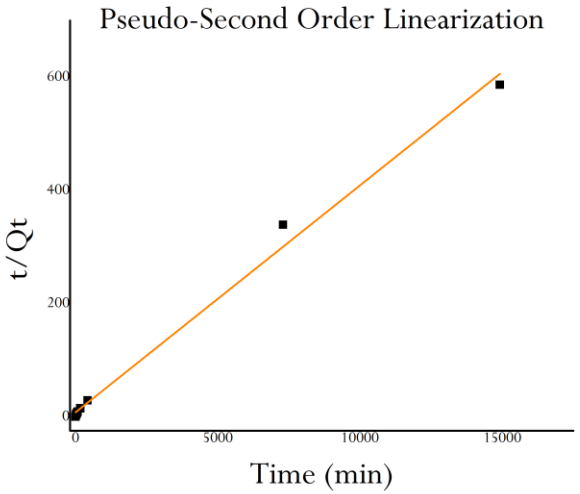
Pseudo-Order Linearized Plots





	Residual $\sum$ Squares	Pearson's r	r^2
Pseudo-First Order	0.06924	-0.92183	0.82830
Pseudo-Second Order	2025.4	0.99718	0.99367

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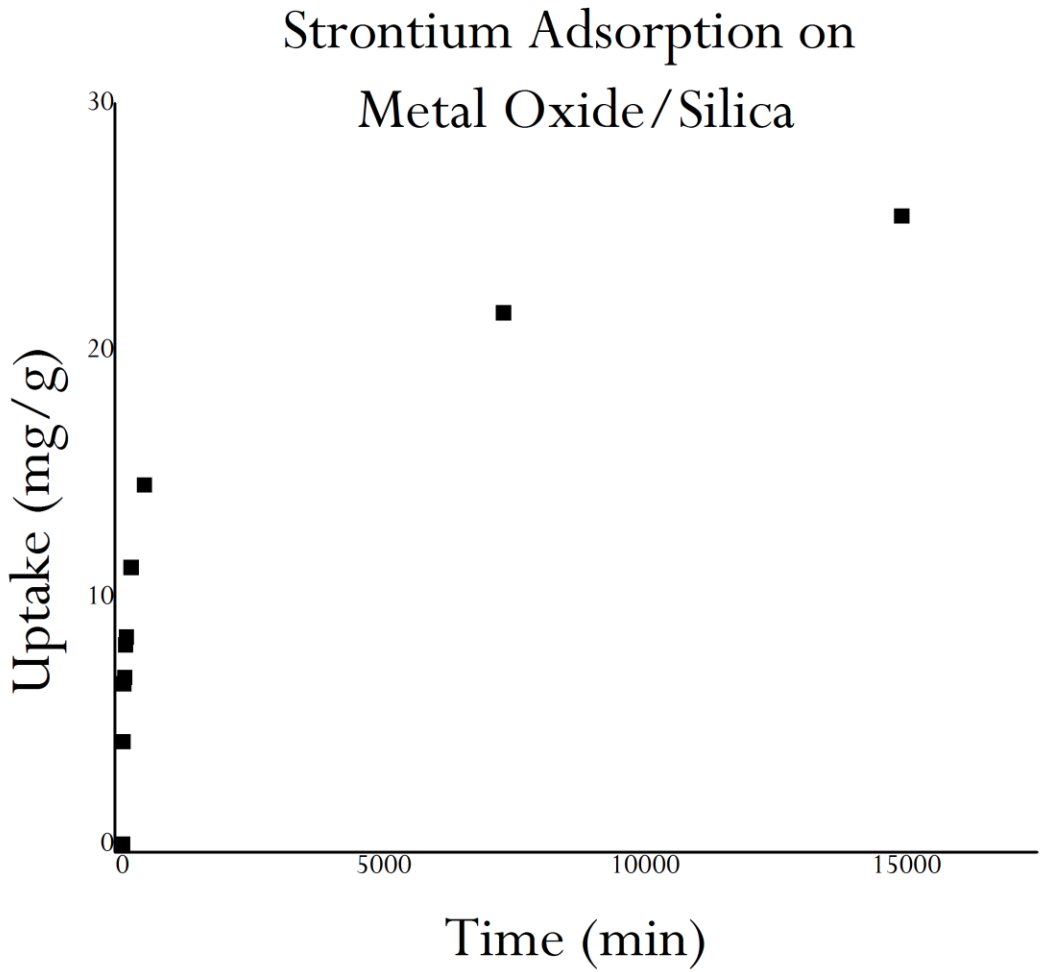
Stronger Fitting Curves with Non-Linear Appraoch



Ratkowsky, D. A. Handbook of Nonlinear Regression Models. *Statistics: Textbooks and Monographs* **107** (1990).

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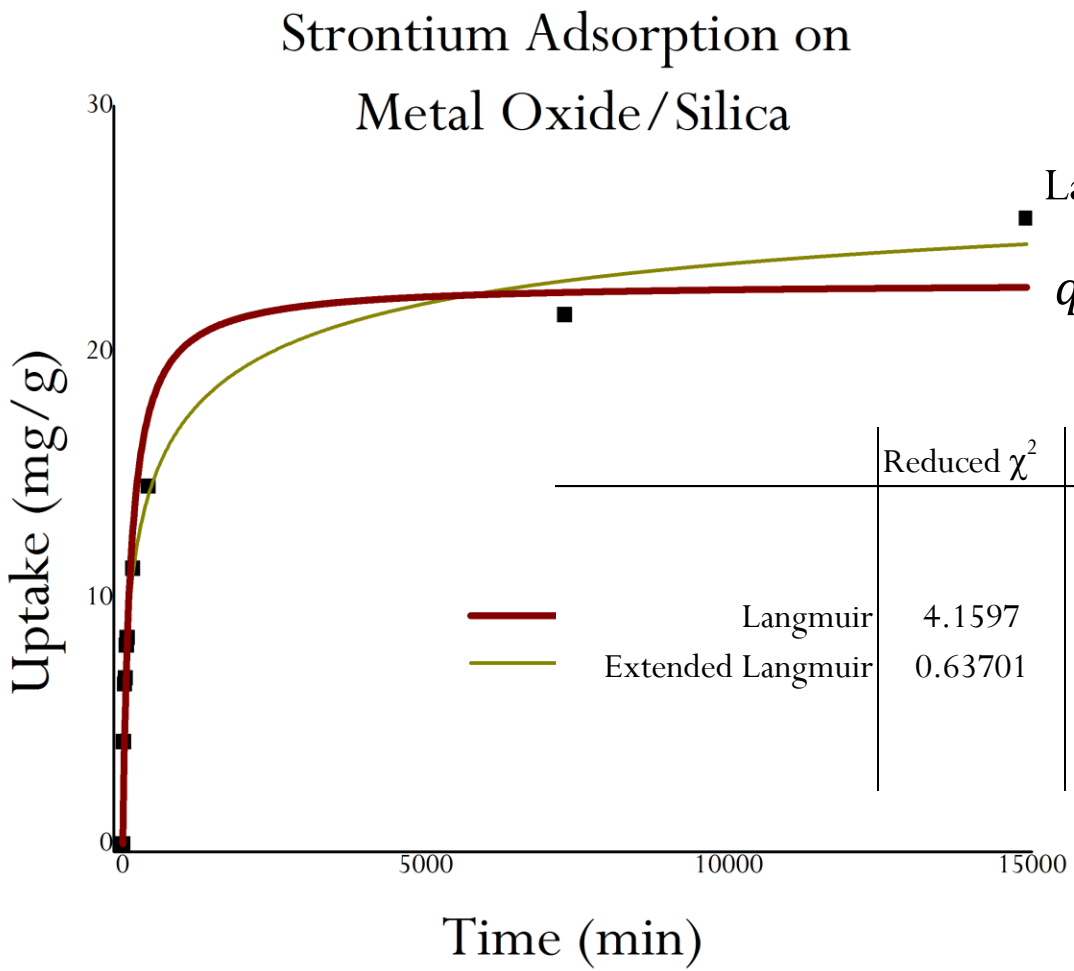
Non-Linear Regression: Langmuir



Langmuir

$$q_t = \frac{q_e k t}{1 - q_e t}$$

Langmuir Extended

$$q_t = \frac{q_e k t^{1-c}}{1 - q_e t^{1-c}}$$

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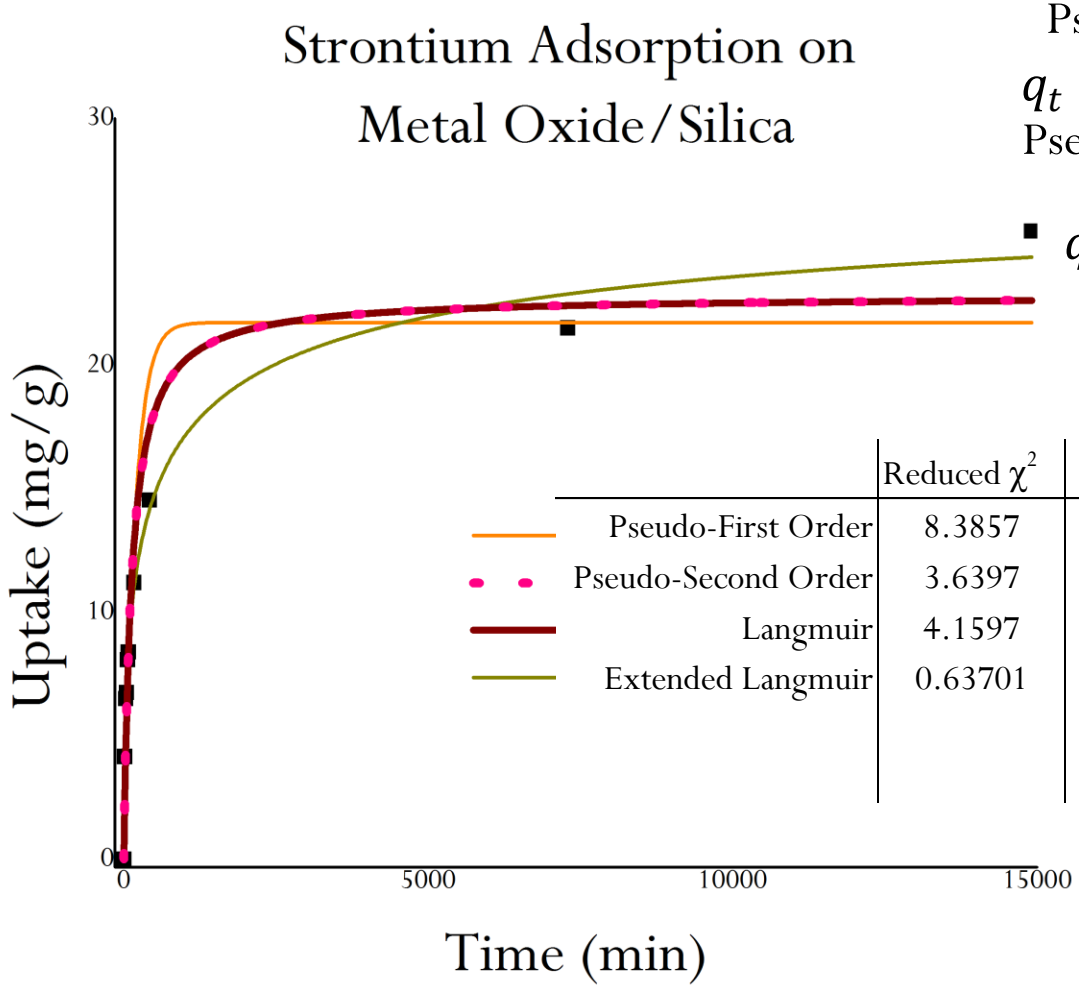
Non-Linear Regression: Pseudo-Order



Pseudo-First Order

$$q_t = q_e(1 - e^{-k_1 t})$$

Pseudo-Second Order

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

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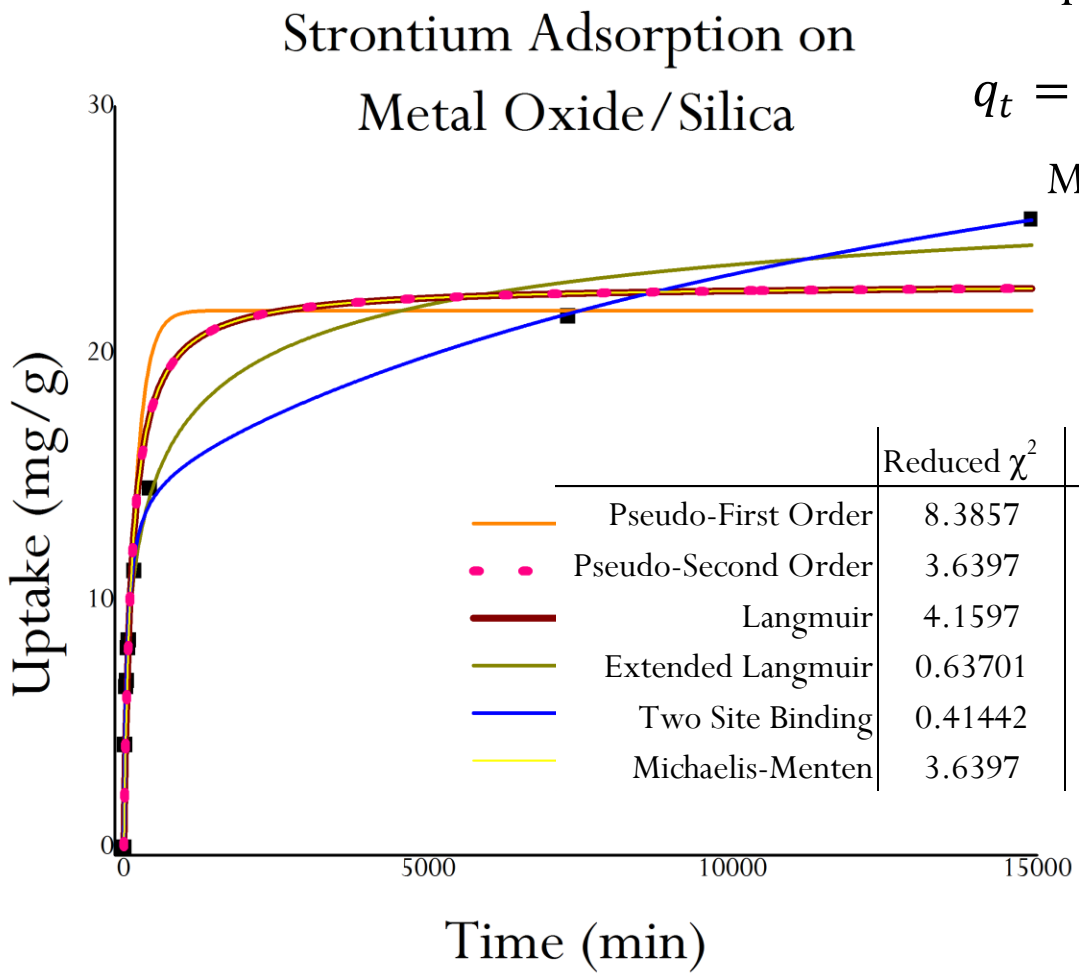
Non-Linear Regression: Reductio ad Absurdum



	Reduced χ^2	r^2
Pseudo-First Order	8.3857	0.86317
Pseudo-Second Order	3.6397	0.94061
Langmuir	4.1597	0.93213
Extended Langmuir	0.63701	0.98803
Two Site Binding	0.41442	0.99324
Michaelis-Menten	3.6397	0.94061

Two Site Binding

$$q_t = \frac{\beta_{max\,a}\, t}{k_a + t} + \frac{\beta_{max\,b}\, t}{k_b + t}$$

Michaelis-Menten

$$q_t = \frac{q_e t}{k_m + t}$$

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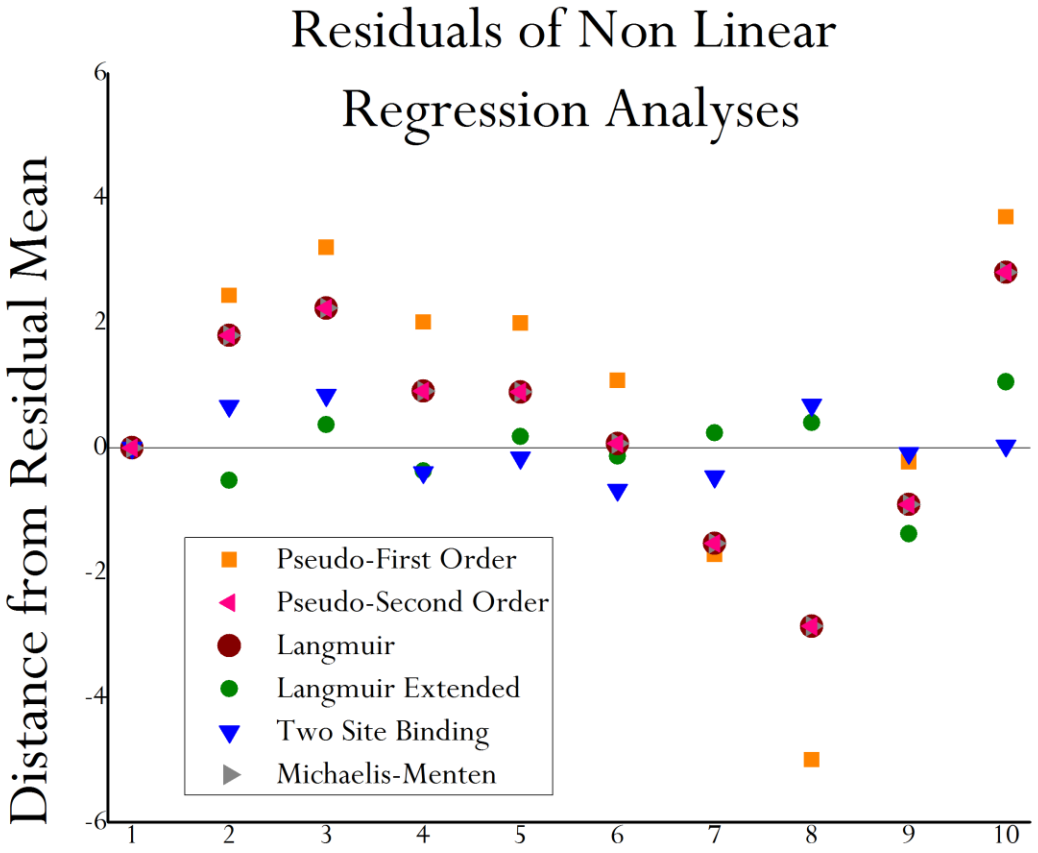
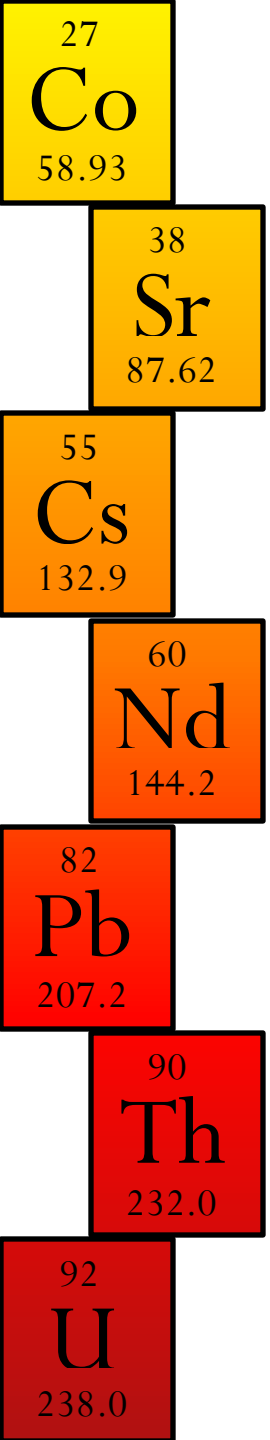
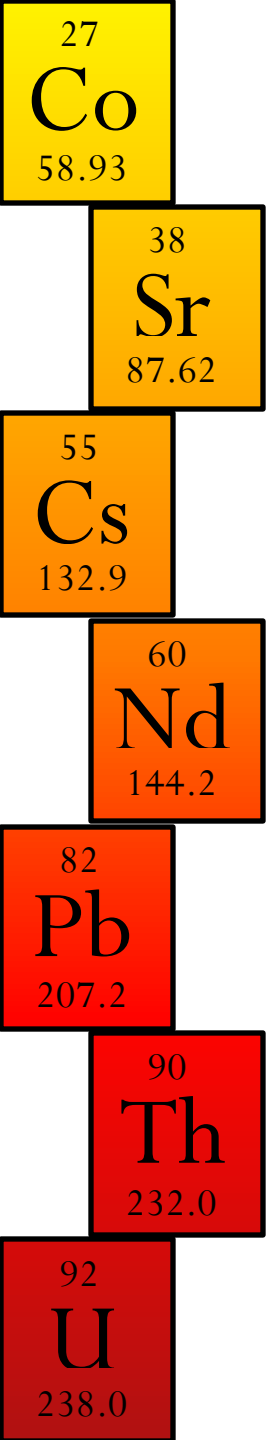
Non-Linear Regression Residual Plots





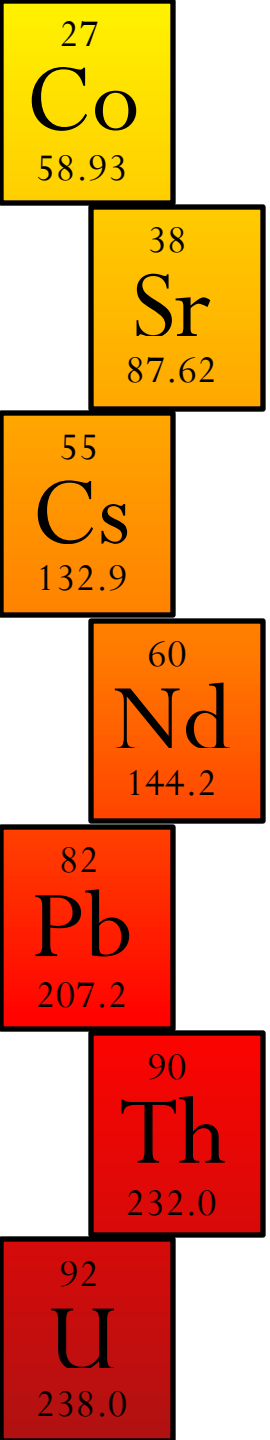
Efficacy of Metal Oxide Adsorbant

	Mw g/mol	Rel. Mass Abs. mg/g	Rel. Moles Abs. µmol/g	Rate Constant g/mgmin
Cobalt	58.93	93.9	1594	7.03E-01
Strontium	87.62	30.3	346	3.09E-04
Cesium	132.9	77.1	332.3	3.72E+00
Neodymium	144.2	183	788.4	5.65E-04
Lead	207.2	83.8	361.1	2.47E-01
Thorium	232	244	1050	6.30E-04
Uranium	238	434	1872	2.16E-04



Conclusions

- Metal oxide provided good uptake of heavy metals from aqueous environments.
- The metals probably deposit in single layer systems by an ion exchange mechanism.
- Non-linear models predict the relationship of time dependent data points well.
- Linearization issues outweigh usefulness of simplicity in this case.



Acknowledgements

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Shoaib Shaikh

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Oklahoma Center for the Advancement of Science and Technology