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On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems

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ABSTRACT

Simulated pseudo-second-order kinetic adsorption data were analyzed by different methods of least-squares regression. The methods used were non-linear regression and four linearized forms of the pseudo-second-order equation. The simulated data were compromised with three different homoskedastic and heteroskedastic error distributions. In the presence of all types of error distributions, non-linear regression was the most robust method and provided the most accurate and efficient estimates of the kinetic parameters.

1. Introduction

Adsorption is the most commonly used technique for the treatment of industrial wastewaters. For practical applications of adsorption such as process design and control, it is important to model the adsorption rate and to establish the time dependence of adsorption systems under various process conditions. Many mechanistic models have been suggested to describe the adsorption kinetics. Two-resistance models, such as the film-solid model [1], the film-pore model [2], and the branched pore model [3], give detailed analysis of the adsorption dynamics. However, these models are presented as partial differential equations and their solution needs dedicated computer programs and extensive computer time. Therefore, it is impractical to use these models in industrial-plant simulations because in industry it is preferred to have more simple relations that can be solved quickly and easily. Even in the area of research, most researchers prefer to use simple lumped kinetic-models to analyze their experimental results. At the present time, Boyd's film-diffusion [4] and Weber's intraparticle-diffusion [5] are the two most widely used models for studying the mechanism of adsorption. However, in spite of their apparent simplicity, the application of both the film-diffusion and the intraparticle-diffusion models often suffers from uncertainties caused by the multi-linear nature of their plots [6].

Another approach to the modelling of adsorption kinetics is the use of pseudo-kinetic models that simulate the overall rate of adsorption. In recent years, Ho presented a model that described adsorption, which provided a novel idea to the second-order equation called a pseudo-second-order (PSO) rate expression [7,8]. The PSO kinetic equation of Ho based on adsorption capacity may be expressed in the form:

$$\frac{dq_t}{dt} = k(q_m - q_t)^2 \quad (1)$$

Table 1
Pseudo-second-order kinetic model linearized forms.

Type	Linearized form	Plot	Effects of linearization
Linear 1	$\frac{t}{q} = \frac{1}{kq_m^2} + \frac{1}{q_m}t$	t/q vs. t	- Reversal of relative weights of data points because of $1/q$ in the dependent variable - t in both dependent and independent variables, leading to spurious correlation
Linear 2	$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{kq_m^2}\right)\frac{1}{t}$	$1/q$ vs. $1/t$	- Reversal of relative weights of data points because of $1/q$ in dependent variable - Independent variable is $1/t$, leading to distortion of error distribution
Linear 3	$q = q_m - \left(\frac{1}{kq_m}\right)\frac{q}{t}$	q vs. q/t	- q in both dependent and independent variables, leading to spurious correlation - The presence of q in the independent variable (q/t) introduces experimental error, violating a basic assumption in the method of least squares - $1/t$ in independent variable, leading to distortion of error distribution
Linear 4	$\frac{q}{t} = kq_m^2 - kq_m q$	q/t vs. q	- q in both dependent and independent variables, leading to spurious correlation - The presence of q in the independent variable introduces experimental error, violating a basic assumption in the method of least squares

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Table 2
Definition of the measurement-error models used.

Measurement-error model	Definition
MEM-I	Independent random error in q with constant variance
MEM-II	Independent random error in C with variance proportional to C Error in q dependant on error in C according to Eq. (5)
MEM-III	Independent random error in C with constant variance Error in q dependent on error in C according to Eq. (5)

where k is the rate constant of pseudo-second-order adsorption ($g\ mg^{-1}\ min^{-1}$), q_m is the amount of solute adsorbed at equilibrium ($mg\ g^{-1}$), and q_t is the amount of solute adsorbed at time t ($mg\ g^{-1}$). Integrating Eq. (1) for boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$ gives:

$$q_t = \frac{q_m^2 kt}{1 + q_m t} \quad (2)$$

Table 3
Percentage errors in estimated values of q_m and k obtained from linear and non-linear regression calculations. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q and C values. (MEM-I). ε_q: % error in estimated value of q_m, ε_k: % error in estimated value of k.

Error variance (% of q_m)		Non-linear		Linear 1		Linear 2		Linear 3		Linear 4	
		ε_q	ε_k	ε_q	ε_k	ε_q	ε_k	ε_q	ε_k	ε_q	ε_k
2	Mean	0.29	−1.60	−0.14	1.50	−71.18	2.55	1.75	−6.02	−1.13	2.97
	Standard deviation	0.92	3.99	1.39	7.77	217.7	67.37	2.39	11.76	3.06	12.68
	Variance	0.84	15.89	1.93	60.31	47,407	4539	5.69	138.4	9.38	160.7
	Median	0.34	−2.36	−0.26	1.78	1.97	3.43	1.42	−1.42	−1.36	5.40
5	Mean	0.25	−0.58	3.70	11.08	−21.79	15.73	7.25	−35.48	−3.86	8.09
	Standard deviation	1.45	7.25	18.32	54.19	252.7	106.4	8.78	55.73	8.03	27.16
	Variance	2.11	52.51	335.6	2937	63,855	11,311	77.15	3105	64.50	737.8
	Median	0.45	0.31	−0.05	4.93	7.29	24.91	4.32	−12.08	−1.64	6.93
10	Mean	0.30	−1.33	0.27	65.36	10.37	34.81	9.81	−50.46	−3.48	1.96
	Standard deviation	2.20	10.27	5.90	236.5	170.6	607.5	6.66	50.58	10.36	34.54
	Variance	4.83	105.4	34.83	55,964	29,099	3.69×10^5	44.38	2559	107.3	1193
	Median	−0.03	0.09	−−0.38	2.69	28.47	−50.38	9.96	−42.76	−0.62	2.50
20	Mean	−1.19	5.48	−13.07	3.74	53.84	−113.9	15.53	−113.3	−8.61	11.14
	Standard deviation	3.23	13.11	48.60	81.88	81.21	212.0	10.11	126.8	15.95	41.22
	Variance	10.41	171.9	2362	6704	6596	44,927	102.3	16,076	254.3	1699
	Median	−1.36	7.56	−2.80	17.10	41.40	−155.2	16.41	−78.41	−5.59	18.59

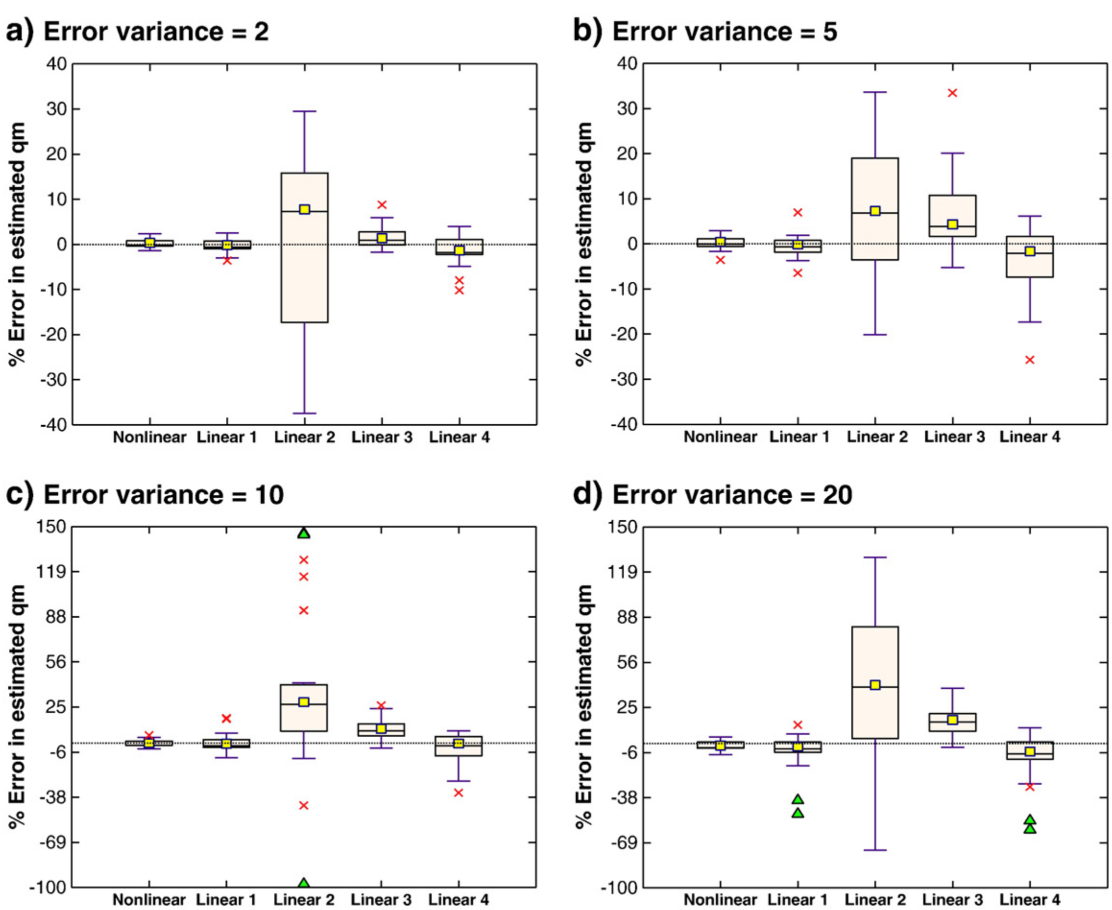

Fig. 1. Box plots for the percentage error in estimation of q_m by different methods of regression of synthetic PSO data at different levels of error variance. Synthetic kinetic data were obtained by adding independent random errors to ideal pseudo-second-order q and C values. (MEM-I).