REVIEW ARTICLE

Comparison Between Pseudo- first-order and Pseudo-second-order of Linear and Nonlinear Equations Adsorption Kinetic Models for the Removal of Amoxicillin (AMX) onto Hydrogel

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ABSTRACT

An experiments conducted on kinetic model for the sorption of amoxicillin (AMX) by hydrogel. We studied the kinetics pseudo first-order (PFO) and kinetics pseudo second order (PSO) by linear and a nonlinear process. Nonlinear PFO and nonlinear PSO term evenly on prophesy that the qe value (qe(exp) =qe(cal) = 2.8999 and 2.947 mg/g) are at the same order comparative with linear PFO and PSO was applied straight line, the value of R^2 is 0.9507 and 0.9707 and the qe value (qe(exp) =qe(cal) = 1.4420 and 2.4913 mg/g) at the same order. The sorption method was found to follow a both nonlinear kinetic model PFO and kinetic model PSO. Linear way was found to check only the hypothesis instead of verifying the model kinetic. Nonlinear regression way was found to be the more appropriate way to estimation the parameters kinetic model.

Keyword: Adsorption, Amoxicillin (AMX), Hydrogel, Kinetics model, Linear model, Nonlinear model, Pseudo-first order, Pseudo-second order.

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INTRODUCTION

Adsorption methods are proved to be very affective way for the elimination of AMX drug from aqueous solution. hydrogel is the utmost usually utilized adsorbent for the elimination of drug from its waste water.[1-3] The adsorption process is used in a wide field because the adsorption process is considered one of the best, easiest, least expensive and very effective ways to get rid of the utmost dangerous contaminant in the aquatic environment, the most important of these pollutants are pharmaceutical, drug, heavy metals, dyes and organic pollutants.[4,5] Hydrogel is the best surface used to remove these pollutants. Most adsorption studies are based on isothermal, kinetic, and thermodynamic processes. Adsorption process, it is significant to analyze the kinetic data to estimation the kinetic properties.[6-8] The utmost generally utilized model expressions kinetic to clarify the solid/liquid adsorption methods are the kinetic models of PFO and PSO. usually utilized to explain adsorption result obtain under non-equilibrium conditions.[9-12] In late years, the linear equations of PFO and PSO were great utilized to estimation the utmost fit kinetic for the adsorption method. When utilizing the linear kinetics adsorption investigational should be linear for the linear regression least-squares to valuation of the model factor. It has been reported that conversion of equations nonlinear to equations linear forms alter implicitly their error structure in the measurement of parameter of model kinetic.[12-14] As data, one may get several kinetic factors when utilizing several model equations for a given adsorption methods. In this study compare between of two kinetic models (PFO and PSO) for a best interpretation of adsorption experiment of AMX onto hydrogel. Too a comparison regression of nonlinear, linear way of determining model kinetic.

EXPERIMENTAL PART

Preparation of Hydrogel

The hydrogel preparation process is based on free radicals. Where 2 mL was taken from ethanol, it was dissolved in (0.1 g) of the polymer and (2 mL) of acrylic acid in the presence of nitrogen gas. After that, (0.02) was added during a whole hour, potassium per-sulfite was gradually added, then this mixture was placed in a water bath for half an hour to complete the polymerization process at a temperature (50°C) The polymer was prepared and washing with DW several times, dried and ground to obtain the powder used in this experiment.

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Batch Adsorption Studies

Experiments adsorption Kinetic were conducted to establish the effect of time on the adsorption method. The mode linear and model non-linear were utilized to explain the curves of the kinetics. To study the adsorption of the AMX onto hydrogel at different concentrations were used, that 0.05 g of hydrogel adding in 100 mL of solution AMX drug. The conical was put in shaker water bath to stirring the AMX drug solution. The agitation speed at 200 rpm through the experiment. and estimation the adsorption time at one hr. taken 5 mL from AMX drug solution and analyzes the concentration via utilizing a UV-visible spectrophotometer at 277 nm. The quantity of adsorption at time t denoted as q t(mg/g) was studied in equation (1):[15,16]

$$qt = V_{sol}.(C_o - C_t)M \qquad (1^*)$$

C_o and Ct (mg/L) conc. of AMX drug at primary and t any time concentration at the same order, M(g) Weight hydrogel.

RESULTS AND DISCUSSION

Pseudo-First-Order

Term Lagargren offered the of model first-order for n =1 as appear in equation

$$\frac{dqt}{dt} = k_1(qe - qt)^n \ (2*) \qquad (2^*)$$

where q t the quantity of AMX drug adsorbed at any time (mg/g)., q e the quantity of AMX drug adsorbed on to hydeogel at equilibrium (mg/g), K1 constant rate of model P-FO.

Integrating equ. (2) for conditions boundary (t = 0, qt = 0 and t = t, qe =qt) leads to give linear equation:

$$Ln(q_e-q_t)=lnq_e- K_1t \qquad (3^*)$$

Which can be rearranged in a nonlinear.

$$q_t=q_e(1 - e^{-K1.t}) \qquad (4^*)$$

Pseudo Second Order

Term of the PSO adsorption reaction prosses via Ho *et al.*[9] was calculate in Eq. (5), n = 2:

$$\frac{dqt}{dt} = k_2(qe - qt)^2 \qquad (5^*)$$

The equation integration of boundary at (t = 0, qt = 0 and t = t, qe = qt) appear in Eq.

$$q_t=\frac{q_e^2\, K_2.t}{q_e\, K_2.t+1} \qquad (6^*)$$

qe,qt (mgg^{-1}) adsorbate quantity adsorbed at equilibrium and at any t(min), at the same order and k_2 rate constant. Eq. (8) can be rearranged to get the equation linear:

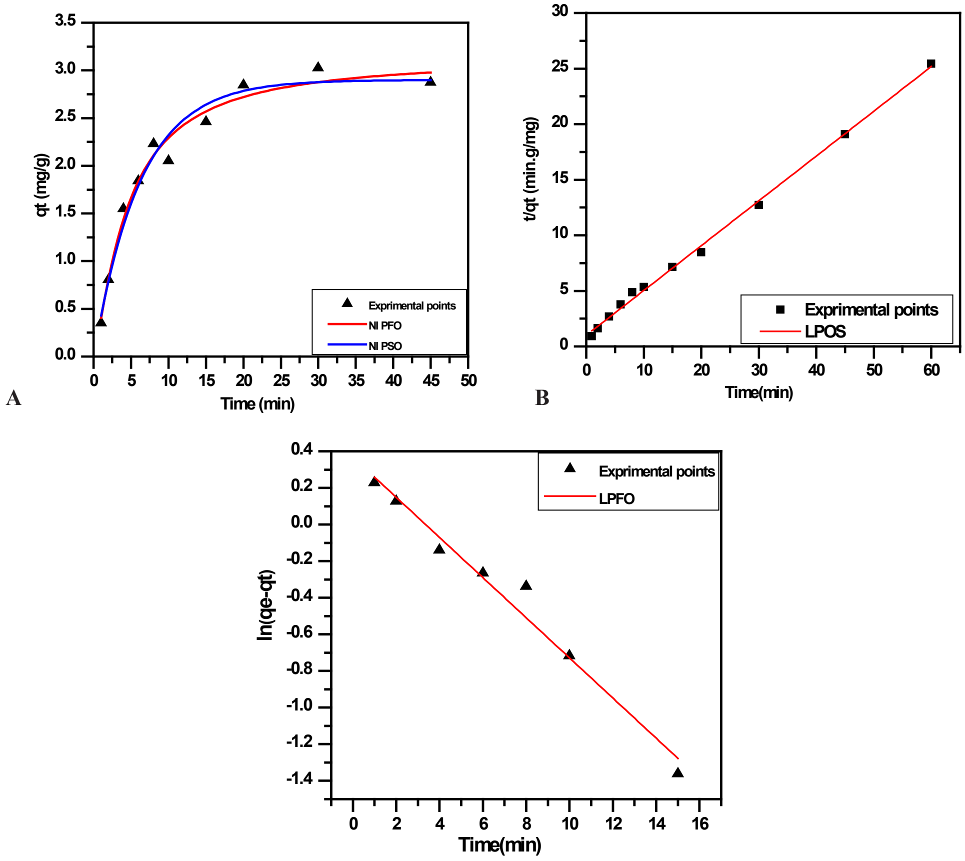

Figure 1: Non-Linear (A) linear (B) P-FO (C) P-SO kinetics models of the adsorption of AMX on to hydrogel

Table 1: Kinetic model PFO and PSO for linear and non linear equation

Kinetic model	*Equ*	*Linear equation*	*plot*	*Parameters*
Pseudo First -order	1	$\mathrm{Log}\ (q_e\text{-}q_t)=\log(q_e)-(k1.t/2.303)$	$\mathrm{Log}\ (q_{e,exp}\text{-}q_t)$ vs t	$K=-2.303*\mathrm{slope}$
	2	$\mathrm{Ln}\ (q_e\text{-}q_t)=\ln(qe)-Kt$	$\mathrm{Ln}\ (q_{e,exp}\text{-}q_t)$ vs t	$K=-\mathrm{slope}$
Type 1 Pseudo second-order	3	$\frac{1}{q}=\frac{1}{K2q_e^2}+\frac{1}{q_e}t$	1/q vs t	$q_e=\frac{1}{\mathrm{slope}}$ $K_2=\frac{slope2}{\mathrm{Intersept}}$
Type 2 Pseudo second-order	4	$\frac{1}{q}=\left(\frac{1}{K2q_e^2}\right)\frac{1}{t}+\frac{1}{q_e}$	1/q vs 1/t	$q_e=\frac{1}{\mathrm{Intersept}}$ $K_2=\frac{Intersept2}{\mathrm{Slope}}$
Type 3 Pseudo second-order	5	$\frac{1}{t}=\left(\frac{K2q_e^2}{q}\right)+\frac{K2q_e^2}{q_e}$	1/t vs 1/q	$q_e=\frac{Slope}{\mathrm{Intersept}}$ $K_2=\frac{Intersept2}{\mathrm{Slope}}$
Type 4 Pseudo second-order	6	$\frac{q}{t}=K2q_e^2+\frac{K2q_e^2}{q_e}$	q/t vs q	$q_e=\frac{Intersept}{\mathrm{Slope}}$ $K_2=\frac{slope2}{\mathrm{Intersept}}$
Type5 Pseudo second -order	7	$\frac{1}{(q_e-q)}=\frac{1}{q_e}+K2.t$	$1/(q_{e,exp}\text{-}q)$ vs t	$q_e=\frac{1}{\mathrm{Intersept}}$ $K_2=\mathrm{slope}$
Nonlinear equation				
Pseudo First -order	8	$q_t=q_e[1-\exp^{(kf^{t})}]$	q_t vs t	
	9	$\frac{Ct}{Co}=1-\frac{ms\ qe}{co}(1-e^{-kt})$	$\frac{Ct}{Co}$ vs t	
Pseudo Secound -order	10	$q_t=\frac{K2qe2t}{1+K2qet}$	q_t vs t	
	11	$\frac{Ct}{Co}=1-\frac{ms\ qe}{co}\left(1-\frac{K2qet}{1+K2qet}\right)$	$\frac{Ct}{Co}$ vs t	

$$\frac{1}{q_t}=\frac{1}{K_2\,q^2{}_e}+\frac{1}{q_e}t\ (7*)$$

After integration via utilizing the boundary conditions q t= 0 at t = 0 and q t= q t at t = t, equation 1, 2 might rearranged to find the nonlinear, linear for kinetic Equations 1-7 as appear in Table 1

Study Adsorption kinetics of AMX drug on to hydrogel were used adsorption method, depended of the optimum conditions. Figure 1 appear the experimental kinetics adsorption of AMX drug on to hydrogel at room temperature. Every one of Eq in Table 1 utilized the soft-ware Origin 8.5 to limit the regression nonlinear and linear. It should be noted qe value utilized to appropriate in Eqs. 1, 2, and 7 was value investigational (qe, exp) taken from adsorption equilibrium study.[17,18] Linear regression was the frequently utilized way to locate the better fitted model kinetic and its factor. Equations 1 and 3 are the utmost common forms utilized in new years. thus Table 1 appear that both the non-linear and linear models P-FO and P-SO and linear PSO have several kinds (five kind of PSO linear), whereas linear simple regression might result evaluation of the several parameters. while Eq. 9 and 11 are not utilized, they can be acquired when substituting Eq. 1* in to Eqs. 8 and 10, at the same order. Equations 9 and 11 present the estimation of parameters of kinetic model of adsorption method in our previous studies. as well Equations 8 and 10 too were utilize in some literatures for regression nonlinear.[17,19,20]

The kinetic PSO theoretical and constant qe via a type 1 PSO expression can be determined for the plot of t/q vs t that appear in Figure 1. also the kinetic model PSO K_2 constant and the theoretical qe can be found for the plot of 1/q vs 1/t, 1/t vs 1/q, q/t vs q and 1/(qe − q)vs t for a equation type PSO (2, 3, 4, 5) expressions at the same order. Figure 1 appear the comparative of kinetics model AMX drug onto hydrogel for fit the experimental result by the nonlinear and linear model forms.[21] where q_t,cal and q_t,exp (mg/g) are the calculated and experimental adsorption quantity at time t, at the same order.[22,23] The parameters of kinetic found from nonlinear and linear fitting (Figure 1) as appear in Table 2.

Table 2: Kinetic factor obtained via utilizing the nonlinear, linear kinetic methods

Kinetic model	*Equation*	$q_{e,exp}$ *(mg/g)*	$q_{e,cal}$ *(mg/g)*	K_1 *(min^{-1})*	K_2 *(g.mg^{-1}.min^{-1})*	R^2
Linear PFO	$\mathrm{Ln}\,(q_e-q_t)=\ln(qe)-Kt$	2.988	1.4420	-0.1096	-	0.9507
Non-linear PFO	$q_t = q_e[1-\exp^{(\,k f\,t)}]$		2.8999	0.1609	-	0.9935
Linear PSO	$\frac{1}{q}=\frac{1}{K2q_e^2}+\frac{1}{q_e}t$		2.4913	-	0.9989	0.9707
Non-linear PSO	$q_t=\frac{K2qe2t}{1+K2qet}$		2.947	-	0.1488	0.9899

The plots of nonlinear Pseudo First-order (NL-PFO), Nonlinear Pseudo second-order (NL-PSO), linear Pseudo First-order (LPFO) and linear Pseudo second-order (LPSO) models as appear in Figure 1 (A, B and C). It was made clear that the investigational points conform by model nonlinear P-FO and nonlinear P-SO rather than the model linear P-SO and linear P-FO. Table 2 shown R^2 is almost equal to one. Also, a nonlinear PFO and nonlinear PSO expression predicts the qe value (qe(exp) =qe(cal) = 2.8999 and 2.947 mg/g) at the same order. though, the processing of the same experimental result via the model linear PFO and model linear PSO leads to a data that contradicts the previous one.[24,25] Table 2 and Figure 1 explain that when linear PFO and PSO was useful straight line, the R^2 value is 0.9507 and 0.9707 and the qe value (qe(exp) =qe(cal) = 1.4420 and 2.4913 mg/g) at the same order. Where through the results appear in Table 2 that the values of (R^2) and (qe, exp) of the non-linear model for each of (PFO and PSO) experimental are better than the values of the linear model.[26-28]

CONCLUSION

- Adsorption of AMX drug on to hydrogel was found to be well represented via the kinetics model linear and nonlinear PFO and PSO.
- Kinetic nonlinear was found to be a best way than the linear for predicting the parameter and most favorable kinetics.
- Non-linear method both PFO and PSO kinetics good explain the kinetics of AMX drug on to hydrogel.
- Nonlinear PFO and PSO Term evenly prophesy the qe value (qe(exp) =qe(cal) = 2.8999 and 2.947 mg/g) at the same order.

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