

Short communication

Selection of optimum sorption kinetics: Comparison of linear and non-linear method

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Abstract

Comparison of linear least-squares method and a trial and error non-linear method of estimating the kinetic parameters was examined to the experimental data of methylene blue onto activated carbon. Two most commonly used kinetic equations first order kinetics and pseudo second order kinetics was used to analyze the experimental data. The four different form of Ho's pseudo second order kinetic was also discussed. Present investigation showed that the non-linear analysis method as more appropriate method to determine the rate kinetic parameters.

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1. Introduction

Recently sorption processes are proved to be an effective process for the removal of pollutants from wastewaters [1–6]. Activated carbon is the most commonly used adsorbent for separating the pollutants from the aqueous solutions [1]. The prediction of batch sorption kinetics is necessary for design of industrial adsorption column [2]. The most commonly used kinetic expressions to explain the solid/liquid adsorption are the pseudo first order kinetics [7] and pseudo second order kinetic model [2].

Linear regression was frequently used to determine the best-fit kinetic expression. However depending on the way kinetic equation is linearized, the error distribution changes either the worse or the better. So it will be an inappropriate technique to use the linearization method for estimating the rate kinetic parameters. Thus in the present study non-linear method is used to determine the adsorption kinetic parameters. Also a comparative analysis was made between the linear and non-linear method in estimating the kinetic parameters to the experimental kinetic data of methylene blue sorption onto activated carbon. The problems associated with transforming the non-linear equations to linear form are also reported.

2. Experimental

The dye used the present study Methylene blue, a basic (cationic) dye was obtained from Ranbaxy Chemicals, Mumbai. Dye solutions was prepared by dissolving 275 mg of methylene blue in 1 L of double distilled water. The powdered activated carbon used as adsorbent in the present study was obtained from E-Merck limited, Mumbai. The obtained activated carbon was directly used as adsorbents without any pretreatment. Some of the specifications of the activated carbon used in the present study as supplied by the manufacturer are given by: Substances soluble in water: <1%; substances soluble in HCl: <3%; Cl: <0.2%; SO₄: <0.2%; heavy metals as Pb: <0.005%; Iron (Fe): <0.1%; incomplete carbonization: passes test; methylene blue adsorption: <180 mg/g; loss on drying: <10; residue on ignition: <5%.

Sorption kinetics experiments were carried out using baffled agitators of 2 L capacity for different initial dye concentrations. 1.5 L of dye solution of initial dye concentration 275 mg/L was agitated with 0.66 g of activated carbon at room temperature (32 °C) at a pH of 8 and at a constant agitation speed of 800 rpm. 2.5 mL of samples were pipetted out using 10 mL syringe at different time intervals through a syringe filter (membrane filter 0.45 μm). The concentration in the supernatant solution was analyzed using UV spectrophotometer.

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Table 1
Kinetics and their linear forms

Type	Non-linear form	Linear form	Plot	Parameters
Pseudo I order	$q = q_e(1 - e^{-K_1 t})$	$\ln(q_e - q) = \ln(q_e - K_1 t)$	$\ln(q_e - q)$ vs. t	
Type-1 (PS)		$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	t/q_t vs. t	$q_e = 1/\text{slope}$, $K_2 = \text{slope}^2/\text{intercept}$, $h = 1/\text{intercept}$
Type-2 (PS)	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{1}{q} = \left(\frac{1}{K_2 q_e^2}\right) \frac{1}{t} + \frac{1}{q_e}$	$1/q_t$ vs. $1/t$	$q_e = 1/\text{intercept}$, $K_2 = \text{intercept}^2/\text{slope}$, $h = 1/\text{slope}$
Type-3 (PS)		$\frac{1}{t} = \frac{K_2 q_e^2}{q} - \frac{K_2 q_e^2}{q_e}$	$1/t$ vs. $1/q$	$q_e = -\text{slope}/\text{intercept}$, $K_2 = \text{intercept}^2/\text{slope}$, $h = \text{slope}$
Type-4 (PS)		$\frac{q}{t} = K_2 q_e^2 - \frac{K_2 q_e^2 q}{q_e}$	q/t vs. q	$q_e = -\text{intercept}/\text{slope}$, $K_2 = \text{slope}^2/\text{intercept}$, $h = \text{intercept}$

3. Results and discussions

In the present study, the coefficient of determination r^2 was used to determine the best-fit kinetic expression. The equilibrium data following the linearized form of Lagergren pseudo first order kinetics was obtained from the plot of $\ln(q_e - q)$ versus time, t . The method to determine the kinetic parameters were shown in Table 1. The calculated rate constant, predicted q_e values and the corresponding r^2 values were shown in Table 2. The lower r^2 value of 0.7812 shows that pseudo first order kinetic model is not an appropriate model to explain the sorption kinetics of the present experimental data.

The pseudo second order model can be linearized to at least four different types. The details of these different forms of linearized pseudo second order equations and the method to estimate the pseudo second order rate constant K_2 , q_e are shown in Table 2. Further the initial sorption rate h (mg/g min) can be calculated using the Eq. (1) given by [2]:

$$h = K_2 q_e^2 \quad (1)$$

Out of the different linearized form of pseudo second order model shown in Table 1, type 1 which is actually proposed by Ho and McKay [2] is the most commonly used expression by various researchers for different sorption systems. Table 2 shows the calculated K_2 , q_e and the h value for different linearized form of pseudo second order model. From the Table 2, it was observed that the coefficient of determination r^2 value was different for the different linearized equations. These different outcomes show the real complexities and problems in estimating the rate kinetic parameters by linearization technique. The different outcomes for different linearized form of a single non-linear equation for the same set of experimental data is due to the variation in the error structure upon linearizing a non-linear equation.

Table 2
Kinetic parameters for methylene blue onto activated carbon

	Pseudo I order	Type 1 pseudo II order	Type 2 pseudo II order	Type 3 pseudo II order	Type 4 pseudo II order	Pseudo I order (non-linear)	Pseudo II order (non-linear)
q_e (mg/g)	168.88	365.30	365.971	366.96	367.13	354.712	366.36
h (g/g min)	–	1674.46	1210.896	1114.108	1098.571	–	1178.349
K_2 (g/mg min)	–	0.01254	0.00904	0.00827	0.008151	–	0.00877
r^2	0.7821	0.9999	0.9201	0.9201	0.9106	0.9950	0.9985
K_1 (min^{-1})	0.2945	–	–	–	–	0.2945	–

The error distribution may vary the better or worse depending on the way the equation is linearized. Various outcomes for the four linearized equations are also due to the different axial settings, so that would alter the result of linear regression and influence the determination process [1]. Thus it will be more appropriate to use non-linear method to estimate the parameters involved in the kinetic equation. Also non-linear method had an advantage that the error distribution does not get altered as in linear technique, as all the isotherm parameters are fixed in the same axis.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the respective the coefficient of determination between experimental data and isotherms using the solver add-in with Microsoft's spreadsheet, Microsoft Excel. Fig. 1 shows experimental data and the predicted values using non-linear method for both pseudo first order kinetics and pseudo second order kinetics. Fig. 1 also shows the predicted kinetics from the linearized Lagergren kinetic equation. The obtained rate constant K_1 and the predicted q_e values by non-linear analysis were given in Table 2. For non-linear method, the results from the four pseudo second order kinetic linear equations are the same. By using non-linear method there are no problems with transformations of non-linear pseudo second order equation to linear forms and also they are in the same error structures. Further, from Table 2, it was observed that the r^2 value for pseudo first order kinetics was found to be 0.995, this suggests that the applicability of the first order model to predict the sorption kinetics of the present experimental system. Whereas the lower r^2 value for pseudo first order kinetics showed that it is inappropriate to apply pseudo first order kinetic expression. Previously studies by some researchers showed that the pseudo first order kinetics was proved to be successful where the sorption process was found to be rapid and showed a poor-

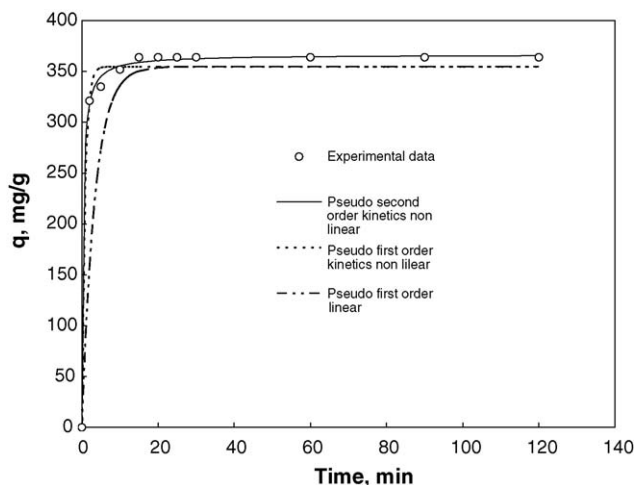


Fig. 1. Adsorption kinetics for methylene blue onto activated carbon (C_0 : 275 mg/L; M : 0.66 g; V : 1.5 L).

fit in the later stages. Kumar et al. [7] showed that the pseudo first order kinetics was found to be successful only for the first 25 min where the solute uptake process was found to be rapid for methylene blue/fly ash system. A similar observation was also reported by Ho and McKay [2] for the sorption of basic dyes onto peat particles. In the present study from Fig. 1, it was observed that the pseudo first order kinetics does not provide any excellent-fit to the experimental data for any period of time interval. However, by non-linear method, it was observed that the same experimental data provide an excellent-fit (Fig. 1) to the pseudo first order kinetic expression for the whole range of sorption period. This observation showed that it is not a correct method to use the linearized form of Lagergren kinetic equation to predict the sorption kinetics, instead non-linear technique will be an appropriate method to obtain the parameters in pseudo first order kinetics. The very high r^2 value for both pseudo first

order and pseudo second order kinetics showed a better-fit to the experimental data. But the relatively a higher value r^2 for pseudo second order kinetics than the pseudo first order kinetics suggests that pseudo second kinetic as an appropriate one to explain the sorption kinetics. Further, the q_e values obtained from the pseudo second order kinetics was found to be nearer the experimental value, suggesting the experimental data was very well represented by the pseudo second order kinetics and also can be used to predict the amount of dye adsorbed at equilibrium conditions.

4. Conclusions

The present communication shows that the search for best-fit kinetic model using linearization technique is not an appropriate technique to predict sorption kinetics. Non-linear method would be an appropriate technique in predicting the sorption kinetics.

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