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Comparison Between Linear and Non-Linear Fitting Methods in Adsorption Process†

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Active carbon was chosen as an adsorbent for adsorption of methylene blue and methyl orange. The effects of initial dye concentration and contact time on adsorption capacity of active carbon were investigated. The pseudo-first-order and pseudo-second-order kinetic models were applied to describe the kinetic data. The Freundlich and Langmuir adsorption models were used to describe adsorption mechanism. In the course of the data processing, linear and non-linear regression methods would be carried out for the best fitting of isotherm. Compared regression results, the character of linear and non-linear fitting methods were studied.

Keywords: Linear fitting, Non-linear fitting, Adsorption, Data processing.

INTRODUCTION

Adsorption has been the subject of extensive research over the past two decades and the fitting of experiment data is carried out to study mechanism[1,2]. Langmuir[3] and Freundlish[4] equations are usually applied in adsorption isotherms; pseudo-first-order[5] and pseudo-second-order[6] equations are applied in adsorption dynamics. In data processing, linear[7, 8] and non-linear fitting[9, 10] are all used and reported widely in literature, but there are some differences between them.

In these study, the adsorption experiments of methyl orange and methylene blue using active carbon as an adsorbent were carried out. The effects of initial dye concentration and contact time on adsorption were studied. Linear and non-linear fitting methods were employed to process data and the results of two methods were compared.

EXPERIMENTAL

Methyl orange (AR M = 327.33 g/mol), methylene blue (AR M = 373.90 g/mol), H_2SO_4 (98 %), NaOH (AR), active carbon (powder, AR) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further purification.

Adsorption experiments: Methyl orange and methylene blue were dissolved in deionized water (pH = 7) to produce stock solutions, respectively.

The dye solutions with different initial concentrations were prepared by diluting the stock solution of each dye with deionized water. The adsorption experiments were carried out at 20 ± 1 ºC in a thermostated shaker. 0.1 g of active carbon and 50 mL of dye solution were mixed in a 100 mL flask and then the flask was shaken for 3 h to attain adsorption equilibrium. After that, a 0.5 mL sample was withdrawn from the flask and diluted with deionized water. The sample was centrifuged at 6,000 rpm for 10 min and the dye concentration of the supernatant liquid was analyzed using UV-VIS spectrophotometer.

In kinetic experiments, 0.5 mL samples were taken from the flask for analysis of the residual dye concentration at regular intervals. All the experiments were carried out in triplicate. The maximum adsorption wavelengths of AO 7, AB 92 and AR 18 were 484, 571 and 506 nm, respectively.

RESULTS AND DISCUSSION

Adsorption kinetics: The non-linear and linear forms of pseudo-first-order were shown as follows:

$$q = q_{eq}[1 - \exp(-k_1 t)] \quad (1)$$

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_{1,ad}}{2.303}t \quad (2)$$

The non-linear and linear forms of pseudo-second-order were shown as follows:

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$$q = \frac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t} \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t \quad (4)$$

Table-1 and Fig. 1 listed the kinetic results of pseudo-first-order and pseudo-second-order. In adsorption studies of methylene blue, the equilibrium adsorption capacity (q_e = 335.8) for methylene blue calculated from eqn. 1 agreed with experimental data q_{exp} = 346.3 mg/g, the value of correlation coefficients (R^2 = 0.989) was high and the sum of square of deviations (Chi^2 = 124.2) was low. The fitting curve was well consonant with experimental data. The results calculated from eqn. 3 were similar. These indicated that non-linear fittings using pseudo-first-order and pseudo-second-order equations were all suitable for adsorption studies of methylene blue.

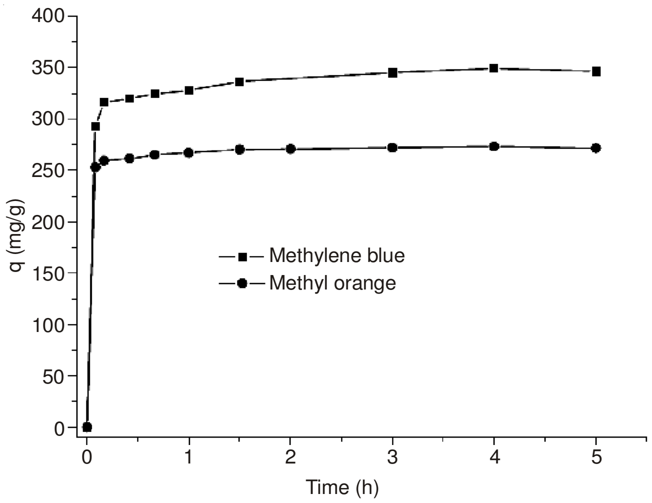

Fig. 1. Effect of contact time on adsorption of methyl orange and methylene blue (initial dye concentration c_0 = 2000 μmol/L)

The q_e (38.0 mg/g) for methylene blue calculated from eqn. 2 deviated considerably from experimental data, the value of R^2 (0.769) was low and the relative deviation (SD = 0.31) was large. These all indicated that linear fitting using pseudo-first-order equation was not suitable for adsorption studies of methylene blue. The q_e (349.3 mg/g) calculated from eqn. 4 agreed with q_{exp} = 346.3 mg/g, the value of R^2 (0.999) was extremely high and the value of SD (6.3E-5) was extremely low. The fitting curve was well consonant with experimental data. These indicated that linear fitting using pseudo-second-order equation was suitable for adsorption studies of methylene blue. In the adsorption studies of methyl orange, the fitting results were similar to methylene blue.

Adsorption isotherm: The non-linear and linear forms of langmuir were shown as below:

$$q_{eq} = \frac{Q_0 b C_{eq}}{1 + b C_{eq}} \quad (5)$$

$$\frac{C_e}{q_{eq}} = \frac{1}{a Q_0} + \frac{C_e}{Q_0} \quad (6)$$

The non-linear and linear forms of Freundlish were shown as below

$$q_{eq} = K_F C_{eq}^{1/n} \quad (7)$$

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Table-2 and Fig. 2 listed the isotherm results of langmuir and Freundlish models. In adsorption studies of methylene blue, the maximum adsorption capacity for methylene blue calculated from eqn. 5 (Q_0 = 437.0 mg/g) was closed to the adsorption amount in experiment (q_{eq} = 481.5 mg/g), but the value of R^2 (0.758) was low. These indicated that the fitting curve was not consonant with the experimental data. The value of K_F (197.7 mg/g) calculated from eqn. 7 deviated from experimental data (q_{eq} = 481.5 mg/g). These indicated that non-linear fittings using Langmir and Freundlish equations were all not suitable for adsorption studies of methylene blue.

The value of Q_0 (478.5mg/g) was closed to the experimental data, the value of R^2 was extremely high and the value of SD was low. The fitting curve was well consonant with experimental data. The value of K_F (196.8 mg/g) calculated from eqn. 8 deviated from experimental data (q_{eq} = 481.5 mg/g). These indicated that only linear fitting using Langmuir model was suitable for adsorption studies of methylene blue. In the adsorption studies of methyl orange, the fitting results were similar to methylene blue, but the non-linear fitting using eqn. 7 was also suitable.

TABLE-1
KINETIC RESULTS OF PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER

Sample		Pseudo-first-order					Pseudo-second-order			
		Non-linear		Linear			Non-linear		Linear	
		Value	Error	Value	Value		Value	Error	Value	Error
Methylene blue	q_e	335.8	3.8	38.0	14.9	q_e	341.9	2.9	349.7	1.5
	k_1	23.8	3.0	0.134	0.026	k_2	0.196	0.033	0.076	0.016
	R^2	0.989	–	0.769	–	R^2	0.995	–	0.999	–
	Chi^2	124.2	–	–	–	Chi^2	53.1	–	–	–
	SD	–	–	0.31	–	SD	–	–	6.3E-5	–
Methyl orange	q_e	268.1	1.5	13.0	3.3	q_e	270.5	1.0	273.2	0.4
	k_1	33.7	3.5	0.098	0.018	k_2	0.571	0.081	0.258	0.057
	R^2	0.997	–	0.789	–	R^2	0.999	–	0.999	–
	Chi^2	19.19	–	–	–	Chi^2	6.06	–	–	–
	SD	–	–	0.21	–	SD	–	–	3.1E-5	–

TABLE-2
ISOTHERM RESULTS OF LANGMUIR AND FREUNDLISH MODELS

Sample		Langmuir					Freundlish			
		Non-linear		Linear			Non-linear		Linear	
		Value	Error	Value	Error		Value	Error	Value	Error
Methylene blue	Q_0	437.0	47.8	478.5	10.3	K_F	197.7	6.9	196.8	4.5
	b	0.114	0.097	0.037	0.017	n	8.77	0.38	8.716	0.294
	R^2	0.758	–	0.997	–	R^2	0.994	–	0.995	–
	Chi^2	7994	–	–	–	Chi^2	89.8	–	–	–
	SD	–	–	0.109	–	SD	–	–	0.0121	–
Methyl orange	Q_0	319.1	13.7	347.2	5.2	K_F	119.3	18.6	98.9	18.7
	b	0.140	0.039	0.026	0.009	n	7.18	1.02	5.88	0.90
	R^2	0.935	–	0.998	–	R^2	0.915	–	0.858	–
	Chi^2	766	–	–	–	Chi^2	1004	–	–	–
	SD	–	–	0.122	–	SD	–	–	0.094	–

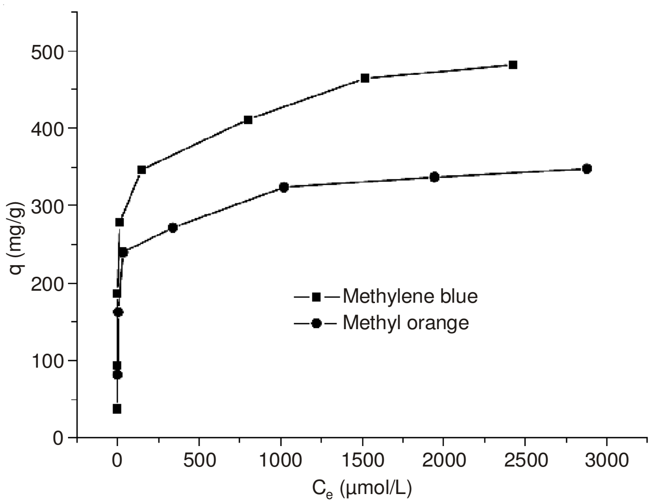

Fig. 2. Effect of initial dye concentration on adsorption of methyl orange and methylene blue

Conclusion

In kinetics studies, the non-linear fittings using pseudo-first-order and pseudo-second-order were all suitable for adsorption studies of methylene blue and methyl orange, the results calculated from pseudo-second-order was slightly better than pseudo-first-order. The linear fitting using pseudo-second-order was suitable and the results from pseudo-first-order were contrary. In isotherm studies, the non-linear fittings using Langmuir and Freundlish were all not suitable for methylene blue and the non-linear fitting using Langmuir was suitable for methyl orange. The linear fittings using Langmuir were suitable for methyl orange and methylene blue. Compared the results of linear fitting with non-linear fitting, the curve of linear fitting was more consonant with experimental data and the results was more closed to experimental value.

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