troplating treatment on ACFs is a useful technique for the removal of noxious gases from the aspect of highly functional metallic catalytic systems.

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Selection of optimum sorption isotherm

Yuh-Shan Ho *

School of Public Health, Taipei Medical University, 250 Wu-Hsing Street, Taipei 11014, Taiwan

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Adsorption has been an effective separation process for a wide variety of applications. The most widely used adsorbent for industrial applications is activated carbon. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes. The most common isotherms applied in solid/liquid system are the theoretical equilibrium isotherm, Langmuir [1], the best known and most often used isotherm for the sorption of a solute from a liquid solution; the Freundlich [2], the earliest known relationship describing the adsorption equation and the Redlich–Peterson [3], the earlier presented, containing three parameters isotherm.

Linear regression was frequently used to determine the most fitted model throughout the years and the method of least squares has been frequently used for finding the parameters of the models. However, transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares [4]. In recent years, several error analysis methods, such as the coefficient of determination, the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors, have been used to determine the best-fitting isotherm [5,6].

In this study, a comparison of linear regression and Chi-square analysis of three isotherms, Langmuir, Freundlich and Redlich–Peterson, have been applied to the experiment of cadmium sorption on tree fern.

Linear regression analysis: The isotherms and their respective linear forms were shown in Table 1 where the linear form of Langmuir-1 was more common. The correlation coefficient (r) and the coefficient of determination (r^2) were shown in Table 2 where the latter has been used to determine the relationship between the experimental data and the isotherms in most studies. In this case, both r and r^2 for both linear forms of Langmuir isotherm were significantly different. If just using the linear form of Langmuir-1 for comparison, Redlich–Peterson isotherm was most suitable for the data followed by Langmuir-1 and then Freundlich isotherm. In contrast, if using the linear form of Langmuir-2, Redlich–Peterson isotherm was still most suitable, but was followed by Freundlich and then Langmuir isotherm. Even though the most suitable isotherm for the dataset was Redlich–Peterson isotherm, the differences between the two linear forms of Langmuir isotherms have significantly affected the result. Three linear equations had different axial settings individually so that would alter the result of a linear regression and influence the determination process.

* Tel.: +886-2-2736-1661x6514; fax: +886-2-2738-4831.

E-mail address: ysho@tmu.edu.tw (Y.-S. Ho).

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Table 1
Isotherms and their linear forms

Isotherm		Linear form
Langmuir-1	$q_e = \frac{q_m K_a C_e}{1+K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$
Redlich–Peterson	$q_e = \frac{A C_e}{1+B C_e^g}$	$\ln\left(A\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B)$

Table 2
Comparison of linear regression correlation coefficient, r, and coefficient of determination, r^2 and non-linear Chi-square test analysis, χ^2

Isotherm	χ^2	r^2	r
Langmuir-1	0.477	0.992	0.996
Langmuir-2	0.398	0.916	0.957
Freundlich	0.0878	0.980	0.990
Redlich–Peterson	0.0878	0.997	0.999

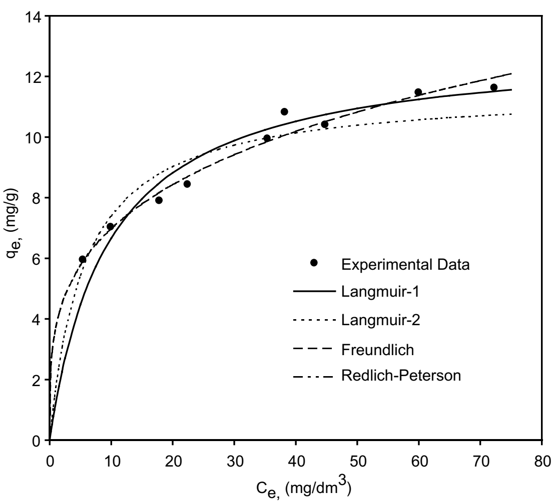

Fig. 1. Theoretical isotherms and experimental data.

Chi-square analysis: The advantage of using Chi-square test was comparing all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{1}$$

where $q_{e,m}$ equilibrium capacity obtained by calculated from model (mg/g) and q_e was the equilibrium capacity (mg/g) from the experimental data. If data from model were similar to the experimental data, χ^2 would be a small number and vice versa. The values of χ^2 of each model were shown in Table 1. In this study, χ^2 of the two Langmuir isotherms were similar where the Redlich–Peterson and Freundlich isotherm exhibited identical and lower χ^2 values than Langmuir and the latter ones were considered to be a better match. The Redlich–Peterson and Freundlich isotherms almost overlapped and seemed to be the best-fitting models for the experiment results from Fig. 1.

Correspondingly, the χ^2 test also showed similar results. Inversely, linear regression has denoted very different outcomes. Consequently, the Redlich–Peterson and Freundlich isotherms were the most suitable models for this sorption system. Unlike the linear analysis, different forms of equation would effect r and r^2 significantly and impact the final determination where non-linear Chi-square analysis would be a method of avoiding such errors.

In this study, we would like to point out that it is not appropriate to use the correlation coefficient (r) or the coefficient of determination (r^2) of linear regression analysis for comparing the best-fitting of Freundlich and both linear Langmuir isotherms. Non-linear Chi-square analysis could be a better method. Freundlich is a special case of Redlich–Peterson isotherm when constants A and B were much bigger than 1. It was clear that both two-parameter Freundlich and three-parameter Redlich–Peterson isotherms were the best-fitting models for the experiment results.

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