Evaluation of Equilibrium Sorption Isotherm Equations

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Abstract: The sorption isotherm is important information for evaluating the ability of an adsorption system to treat the industrial waste water. In this study, eleven datasets from literatures were selected and three two-parameter and three-parameter equations were used to evaluate adsorption systems. Quantitative criteria included six error functions, and the quantitative criterion was residual plots. Isotherm constants differed by linearization and nonlinear regression analysis, especially for the three-parameter equations. The results indicated the inconsistent results of the error functions for selecting the adequate equations. Residual plots were useful to observe the fitting ability of isotherm equations. Temperature has a significant effect on isotherm constants.

Keywords: Isotherm equation, Error functions, Residual plots.

1. INTRODUCTION

Environmental protection has become the basic requirement of industry development. Water or industrial wastewater treatment is an emergency technique for saving the natural environment. Adsorption is a useful technique for purification and separation in treating industrial waste water. With adsorption, pollutants or toxic materials can be removed from aqueous or non-aqueous solutions.

Biological materials have been applied widely used for the adsorption of heavy metals, because of their inexpensive and the ability to bind pollutants. With a constant adsorbate concentration, the absorbent concentration can reach equilibrium at a fixed temperature. The distribution of the concentrations of adsorbate and adsorbent is called the sorption isotherm. The sorption isotherm must be established to evaluate the capacity of an adsorption system. Parameters of sorption isotherm can be used to describe the surface properties of adsorbents and other properties. Factors other than temperature that affected sorption properties included particle size, metal ion [1,2] and pH [3-5].

Four isotherms were selected to compare predictive accuracy with single isotherm data for sorption of three heavy metal ions by pipe bark and to determine binary sorption isotherms [1]. The Langmuir isotherm model was less accurate. cy than other models. Seven sorption models were used to evaluate the sorption of three metal ions from aqueous solution by peat [2]. Six error functions were proposed to evaluate the fitting ability of these models. The Sips equation was the best model for the experimental data for Cu, Ni and Pb. Three isotherms models were used to test tree fern as a sorbent system for removing three types of metal ions [6]. The Langmuir and Redlich-Peterson isotherms could represent the experimental data well. The Langmuir model was extended to predict multi-component sorption data and the fitting ability of the new model was tested [7]. Seven models were tested with the coefficient of determination and the value of the sum of normalized errors for biosorption of ochratoxin A (OA) on yeast biomass as the decontamination agent [8]. The Hill, Freundlich and BET equations were appropriate models.

Many sorption isotherm models have been proposed to assess their ability to fit experimental data. Six two-parameter and nine three-parameter models have been described [9]. Some models were modified to describe multi-component adsorption. More parameters were incorporated into the original form of the model and termed extension isotherm models [1,7,10].

For fitting a nonlinear isotherm model as a linear model, the dependent and independent variables are transformed [2,6,8,11-14]. The transformed dependent variables are then calculated and evaluated by different error equations. The problems in variable transformation and the regression results have been discussed [9,15-17].

The criteria to evaluate the error distribution between the experimental data and the predictive values of isotherm models are called error functions. Nine error functions have been reviewed [9]. Some researchers select one or two criteria, such as the coefficient of determination R^2 and χ^2 [7,11-14,18]. Others adopted several criteria to determine with best performance for all functions [2,8,11].

Common errors in analyzing of sorption isotherm data have been discussed [16]. With linearization, the assumption of experimental error is violated. The variance errors lie in the dependent and independent variables for linear and nonlinear isotherm models. Other errors are abuse of R^2 and neglecting to account for the different degrees of freedom for model comparison [17].

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The error functions are only the quantitative criteria for model evaluation. The qualitative criterion is residual plots [19-20]. However, this criterion has previously been used to evaluate only the assumption of homoskedasity [21].

This study used eleven datasets from the literature to evaluate the appropriate model describing sorption isotherm data. Six isotherm models, including two-parameter and three-parameter equations, were used to evaluate the fitting ability of the models. The quantitative criteria included six error functions and the qualitative criterion was residual plots. The effect of temperature on constants was also exampled.

2. METHODS

2.1. Literature Survey

The eleven datasets, including different temperatures, metal ions and adsorbate range are listed in Table **1**.

2.2. Isotherm Equations

Six isotherms were adopted.

2.2.1. Two-parameter Models

2.2.1.1. Freundlich Isotherm

$$q_e = K_F C_e^{br} \tag{1}$$

where q_e is the amount of solute adsorbed at equilibrium, C_e is the equilibrium concentration, and K_F and br are the Freundlich constants.

Equation (1) can be expressed as an exponential equation,

$$Y = ax^b \tag{2}$$

where a and b are constants.

2.2.1.2. Langmuir Isotherm

$$q_e = \frac{k_L C_e}{1 + a_L C_e} \tag{3}$$

where k_L and a_L are the Langmuir isotherm constants.

Equation (3) can be written as follows:

$$y = \frac{ax}{1 + bx} \tag{4}$$

2.2.1.3. Tempkim isotherm

$$q_e = \frac{RT}{b_T} \text{ In } (A_T C_e)$$

$$= B_T \text{ In}(A_T C_e) \tag{5}$$

where R is the gas constant, T is the temperature in K, and A_T and B_T are the Tempkim isotherm constants.

Equation (5) can be transformed as follows

$$Y = B_T (\text{In } A_T + \text{In } C_e)$$

$$= a + b \text{ In } x \tag{6}$$

2.2.2. Three-parameter Models

2.2.2.1. Redlich-Paterson Isotherm

$$q_e = \frac{K_R C_e}{1 + a_R C_e^B} \tag{7}$$

where K_R, a_R and B are the Redlich-Peterson isotherm constants.

Equation (7) can be written as following:

$$y = \frac{ax}{c + x^b} \tag{8}$$

where $a = K_R/a_R$, b=B and $c = 1/a_R$.

2.2.2.2. Hill Isotherm

$$q_e = \frac{q_{SH} C_e^{nH}}{K_D + C_e^{nH}} \tag{9}$$

where q_{SH}, nH and K_D are the Hill isotherm constants.

Equation (9) can be expressed as follows:

Table 1. Literature Sources Giving Sorption Isotherm Data

Reference	Source	Temperature (K)	C_e (mg/dm^3)	Adsorbent	Adsorbate
1.Ho and Wang [2]	Figure	298	30~240	Tree fern	Cadmium(Ⅱ)
2. Ho [13]	Figure	298	6~75	Tree fern	Cadmium(Ⅱ)
3. Mckay and Porter [7]	Figure	293	0.1~3.8 0.1~3.6 0.1~3.3	Peat Peat Peat	Cd Cu Zn
4. Wahab et al. [15]	Figure	293 303 313 323 333	0.2~1.38	*Posidonia Oceanica* seagrass fibers	Ammonium
5. Wang and Qin [14]	Figure	298	0~75	Rice bran	Cu^{2+}

$$y = \frac{ax^b}{c + x^b} \tag{10}$$

2.2.2.3. Toth Isotherm

$$q_e = \frac{K_T C_e}{(\alpha_T + C_e)^{1/t}} \tag{11}$$

where K_T, α_T and t are the Toth isotherm constants

Equation (11) is expressed as follows:

$$y = \frac{ax}{(c + x)^b} \tag{12}$$

Two models, Sips and Koble-Corrigan isotherms, had the same form as previous equation.

For the Sips model,

$$q_e = \frac{K_s C_e^{Bs}}{1 + \alpha_s C_e^{Bs}} \tag{13}$$

where K_s, B_s and α_s are the Sips isotherm constants.

Equation (13) has the same form as Equation (10), where $a=K_s/\alpha_s$, b= B_s and $c=1/\alpha_s$.

For the Koble-Corrigan model,

$$q_e = \frac{A_k Ce^n}{1 + B_k C_e^n} \tag{14}$$

where A_k, B_k and n are the Koble-Corrigan isotherm constants.

Equation (14) has the same form as Equation (10), where a= A_k / B_k , b= n and c=1/ A_k.

The Sips and Koble-Corrigan models were not be used to evaluate fitting ability.

2.3. Error Functions

2.3.1. Quantitative Criteria

Six quantitative criteria from the literatures were examined [2,7-9,11-14].

2.3.1.1. Coefficient of Determination, R^2

2.3.1.2. Standard Error of Estimate, s

$$s = ((y_i - \hat{y}_i)^2 / n - p)^{0.5} \tag{15}$$

where $\hat{y}_i$ is the predicted value of the isotherm model, y_i is the experimental data, n is the number of data and p is the number of parameters.

2.3.1.3. Average Relative Error, ARE

$$ARE = \frac{100}{n} \sum \left| \frac{y_i - \hat{y}_i}{y_i} \right| \tag{16}$$

2.3.1.4. Hybrid Fractional Error Function, HYBRID

$$HYBRID = \frac{100}{n - p} \sum \left| \frac{y_i - \hat{y}_i}{y_i} \right| \tag{17}$$

2.3.1.5. Sum of Absolute Error, EABS

$$EABS = \sum \left| y_i - \hat{y}_i \right| \tag{18}$$

2.3.1.6. Marquardt's Percent Standard Deviation, MPSD

$$MPSD = 100 \left(\frac{1}{n - p} \sum \left(\frac{y_i - \hat{y}_i}{y_i} \right)^2 \right)^{0.5} \tag{19}$$

2.3.2. Qualitative Criterion

The residual plot is an important criterion to assess the adequateness of a regression model (Draper and Smith, 1981; Myers, 1986). The distribution between the model predictive errors (residuals) versus predictive values is called the residual plots. A residual plot with a clean pattern indicated that the isotherm model has fixed model errors and is not adequate. A residual plot with a uniform distribution represented an adequate model [19-20].

2.4. The Linearization Problems

For some nonlinear isotherm models, data are transformed to linearization for regression analysis easily. However, this process changes the error structure of the data was changed. The Freundlich isotherm model is used to illustrate the violation of the error structure with transformation.

According to the assumption of regression analysis, the error in the dependent variable is additive error.

$$q_{ei} = K_F\, C_e^{br} + e_i \tag{20}$$

where e_i is the additive error of the model.

The regression model for transformed data is as follows:

$$\mathrm{In}(q_{ei}) = \mathrm{In}\, K_F + br\, \mathrm{In}(C_e) + e_i^* \tag{21}$$

The In (q_{ei}) transformed back to the original form results in the following,

$$q_{ei} = K_F C_e^{br}\, \mathrm{Exp}(e_i^*) \tag{22}$$

The error structures of Equations. (20) and (22) are different, that is, data transformation affected the error structure and could also violate the assumption of homogeneous variance.

Considering the problems with linearization, the six isotherm equations used in this study were also studied by nonlinear regression analysis technique.

2.5. Statistical Analysis

Constants were estimated by nonlinear regression analysis with statistical software Sigma plot v10.0 (SPSS Inc., Chicago. IL).

3. RESULTS AND DISCUSSIONS

3.1. Comparison of Constants with Linearization and Nonlinear Regression

The isotherm constants with linearization and nonlinear regression analysis of datasets are listed in Table **2**. Two

Table 2. Comparison of Constants of Linearization and Nonlinear Isotherm Equations

Isotherm Equation	Linearization Method	Nonlinear Regression
Ochratoxin A Adsorption by EX16 Yeast Biomass [8]		
Freundlich		
k_F	0.013	0.017
b_r	0.9625	0.71890
Langmuir		
k_L	0.0163	0.037
a_L	0.109	0.161
Hill		
q_{SH}	0.078	0.071
nH	1.470	1.751
k_D	4.054	3.950
Ochratoxin A adsorption by beta-glucanes [8]		
Freundlich		
k_F	0.016	0.015
Br	0.9709	1.0373
Langmuir		
k_L	0.0226	0.0162
a_L	0.169	0.005
Hill		
q_{SH}	0.174	0.766
nH	1.040	1.087
k_D	8.004	51.324
Isotherms of methylene blue (MB) at 40℃ [16]		
Freundlich		
k_F	32.636	47.612
Br	0.3695	0.2815
Langmuir		
K_L	19.513	13.0203
a_L	0.0758	0.0524
Biosorption of solophenyl brown textile dye by raw *P. Oceanica* seagrass fibers [22]		
Freundlich		
k_F	0.353	0.361
Br	0.4878	0.4826

Table 2 Contd…..

Langmuir		
k_L	0.140	0.132
a_L	0.036	0.033
Redlich-Peterson		
k_R	0.552	1.189
a_R	1.023	2.806
B	0.598	0.548

regression methods produced different constants. For the ochratoxin A (OA) adsorption onto EX16 yeast biomass [8], the br value of the Freundlich equation was 0.9625 for the linearization equation and 0.7189 for the nonlinear equations. The k_L and a_L values of the Langmuir equation were 0.0163 and 0.109 with linearization, and 0.037 and 0.161 for nonlinear equation.

The difference between constants with linearization and nonlinear analysis is presented for the Langmuir and Hill equations with OA adsorption data onto beta-glucanes. The constants of the Hill equation, q_{SH}, nH and $k_{D,}$ were 0.174, 1.040 and 8.004 with linearization and 0.766, 1.087 and 51.322 for nonlinear analysis.

For the constants k_f and br for the Freundlich equation with sorption data of MB at 40℃ [21] and for the constants of Redlich-Peterson equation k_R, a_R and B with biosorption of solophenyl Brown textile dye onto raw *P. Oceanica* seagrass fibers [22], isotherm constants of three-parameter equations significantly different by regression method.

3.2. Three Literatures Datasets

The estimated isotherm constants and error functions for the six isotherm equations for three datasets are listed in Table **3**. For the Ho and Wang data [2], the Toth equation produced the highest R^2 value and the Hill equation had the lowest EABS value. However, the Langmuir equation produced smallest s, ARE, HYBRID and MPSD values. The results for error functions were inconsistent.

The relationship between adsorbate and adsorbent concentrations and the predictive curves of the six equations is presented in Fig. (**1**). Visually determining the fitting ability

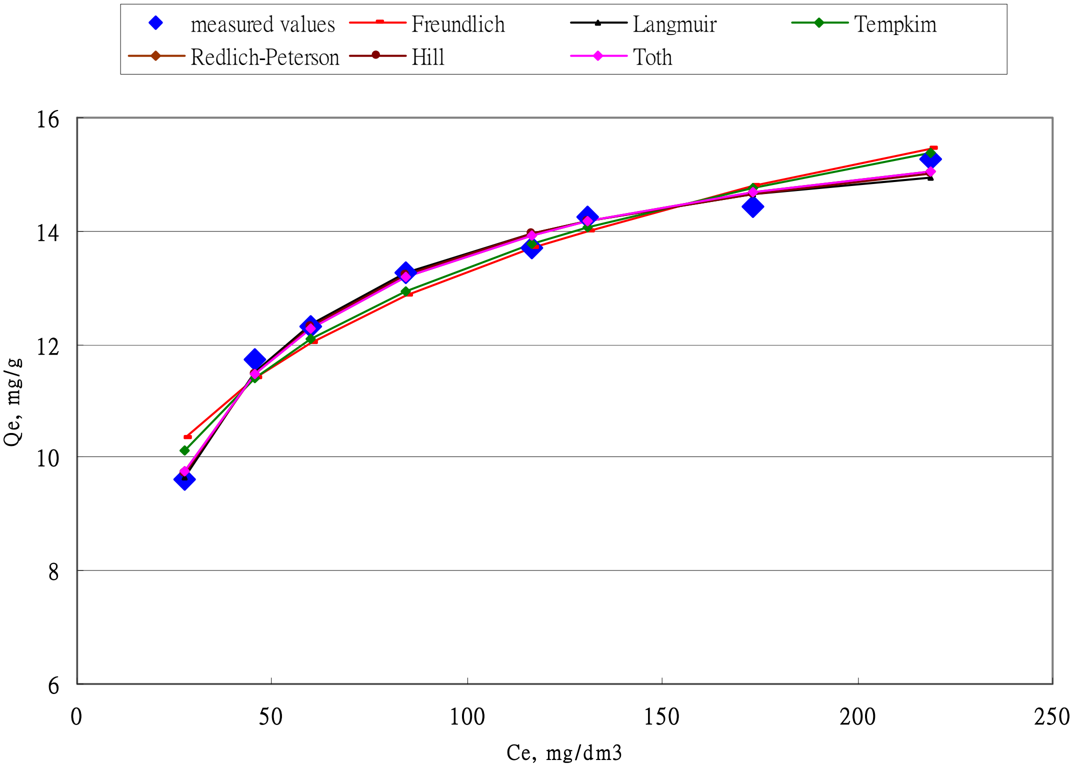


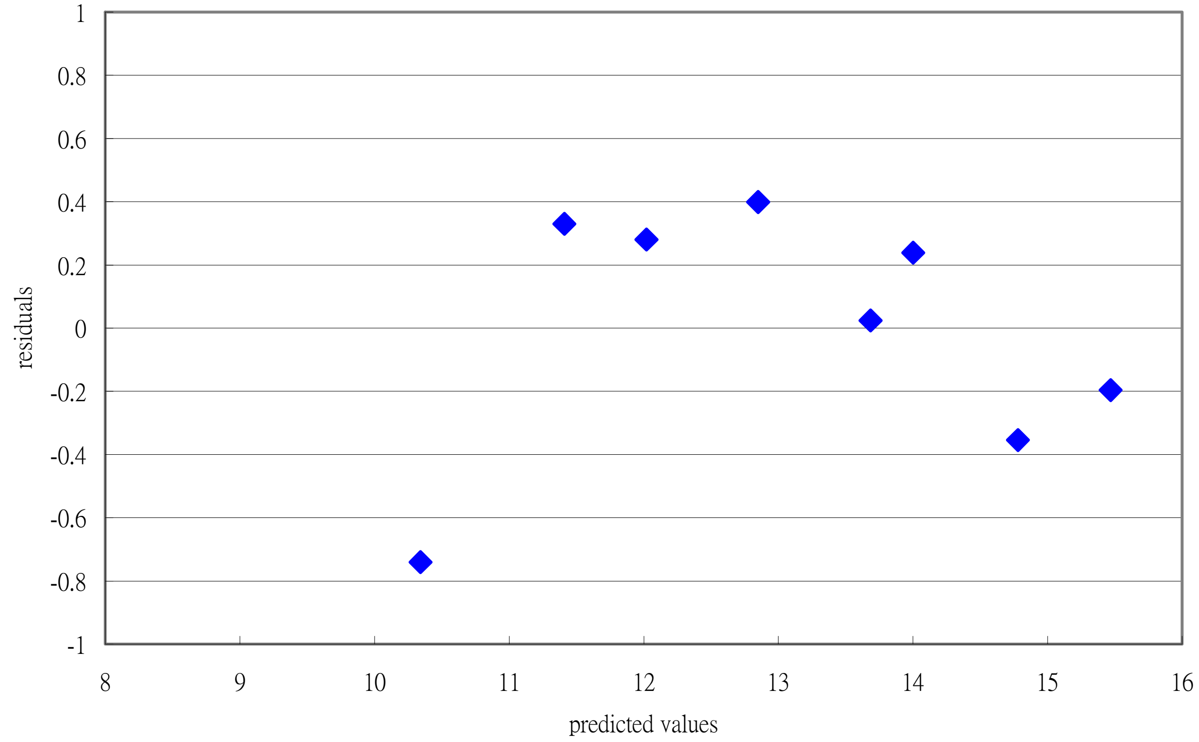
Fig. (1). Sorption isotherms for Ca by tree fern for six isotherm equations.

is difficult. Residual plots provide a useful tool (Fig. **2**). Residual plots showed clean patterns for the Freundlich and Tempkim equations and uniform distributions for the Langmuir, Redlich-Peterson, Hill and Toth equations.

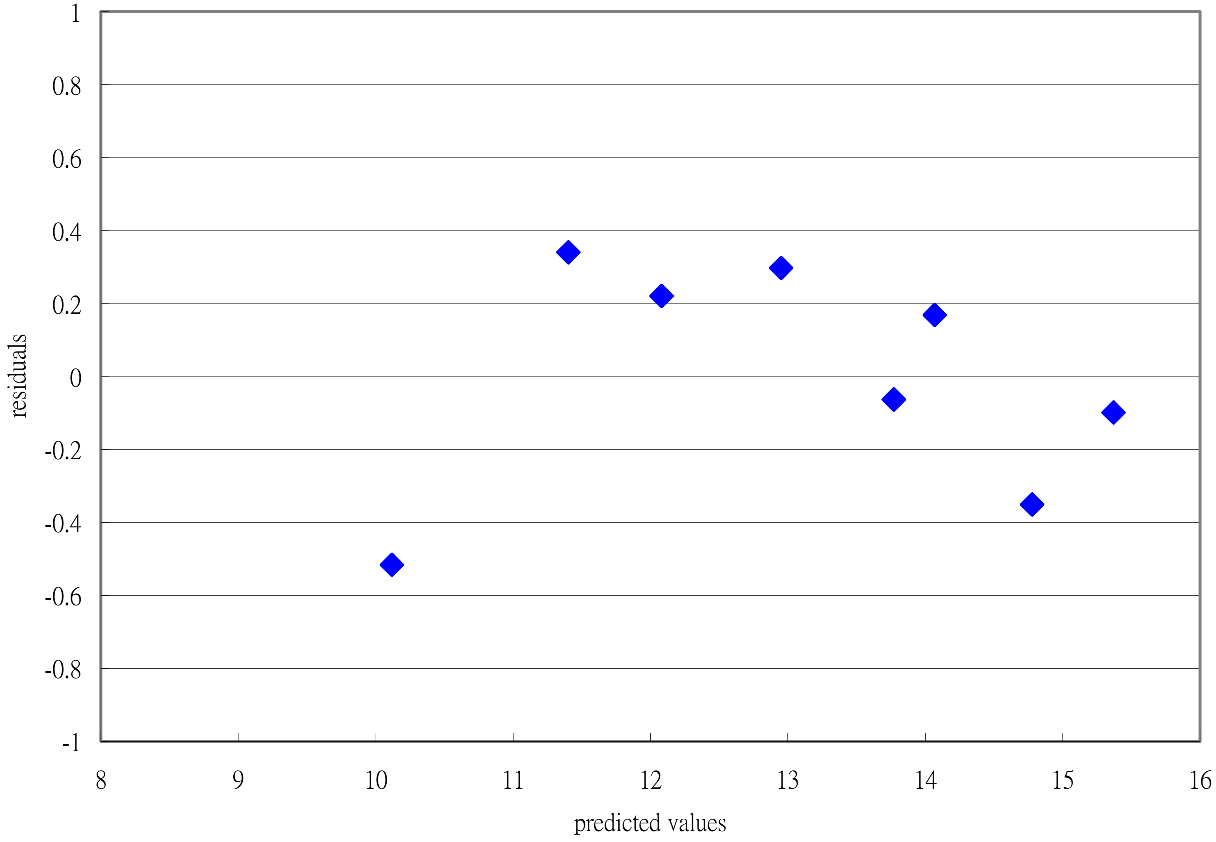
Table 3. Isotherm Constants and Error Functions for Six Isotherm Equations (Data from Three Publications)

Constants and Error Functions	Freundlich	Langmuir	Tempkim	Redlich-Peterson	Hill	Toth
Ho and Wang [12]						
A	5.4306	16.2184	1.7119	13.5384	16.6091	12.8656
B	0.1943	18.6937	2.5353	0.9673	0.9096	0.9593
C				13.5238	14.4257	14.765
R^2	0.9512	0.9874	0.9700	0.9888	0.9880	*0.9891*[1]
s	0.4313	**0.2190**[2]	0.3379	0.2263	0.2346	0.2245
ARE	2.6752	**1.1353**	2.1306	1.5778	1.5564	1.1826
HYBRID	3.5669	**1.5137**	2.8408	2.5245	2.4902	1.8922
EABS	2.5627	2.2033	2.0871	1.2270	**1.2226**	1.2248
MPSD	3.9181	**1.5916**	2.9866	1.7469	1.7748	1.7372
Residual plots	CP[3]	UD	CP	UD[4]	UD	UD
Ho [13]						
A	3.7817	1.9227	2.0001	3.7983	92.3710	3.5794
B	0.2623	6.9994	2.1756	0.7389	0.2664	0.7247
C				2.3508x10^{-8}	18.6475	-0.3109
R^2	0.9717	0.8983	0.9591	0.9717	0.8918	*0.9721*
s	0.7528	0.6693	0.4246	0.3812	0.8765	**0.3785**
ARE	3.2619	6.2111	4.5741	2.5041	2.5536	**2.3084**
HYBRID	4.1938	7.9857	5.8810	3.7562	**3.305**	3.4627
EABS	2.1014	4.5908	2.7069	2.0834	2.1107	**1.9707**
MPSD	8.66643	8.928	5.1166	3.9556	3.9678	**3.8217**
Residual plots	CP	CP	CP	UD	UD	UD
Wang and Qin [14]						
A	9.4144	33.8231	6.4428	26.7573	33.9464	23.6467
B	0.3038	4.8206	6.2993	0.9433	0.9874	0.9171
C				3.2732	4.7806	3.2466
R^2	0.8945	0.9495	0.9497	0.9511	0.9495	*0.9518*
s	3.7984	2.6292	**2.6236**	2.8330	2.8798	2.8139
ARE	29.5650	**11.4088**	12.7038	13.3965	11.6938	13.4340
HYBRID	39.4210	**15.2117**	16.9383	21.4344	18.7110	21.4944
EABS	23.6035	**15.1628**	15.4907	15.7916	15.2741	15.7410
MPSD	5.5658	**15.2408**	17.0818	19.8192	17.0822	19.8702
Residual plots	CP	UD	UD	UD	UD	UD

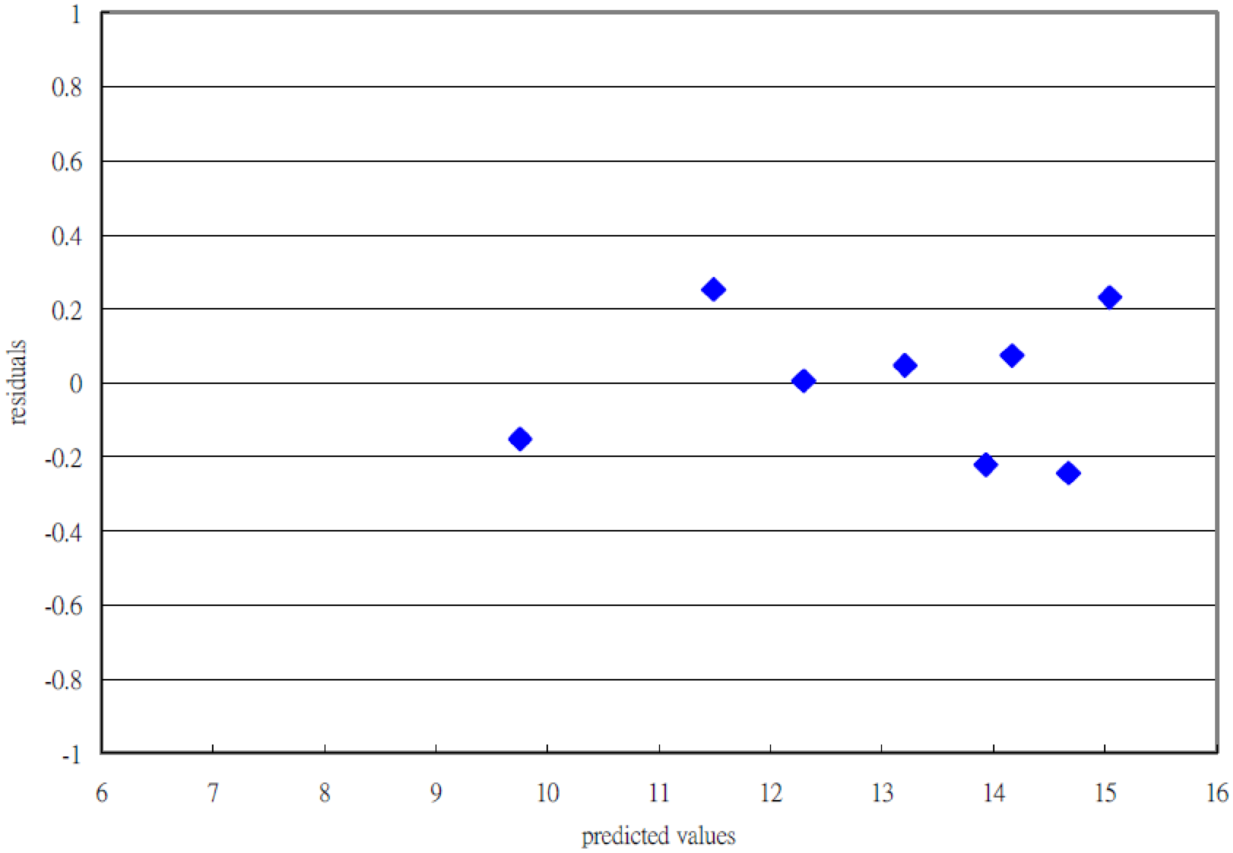
1. Letters in italics represent maximum value.
2. Letters in bold represent minimum value
3. CP: clean pattern of residual plots
4. UD: uniform distribution of residual plots



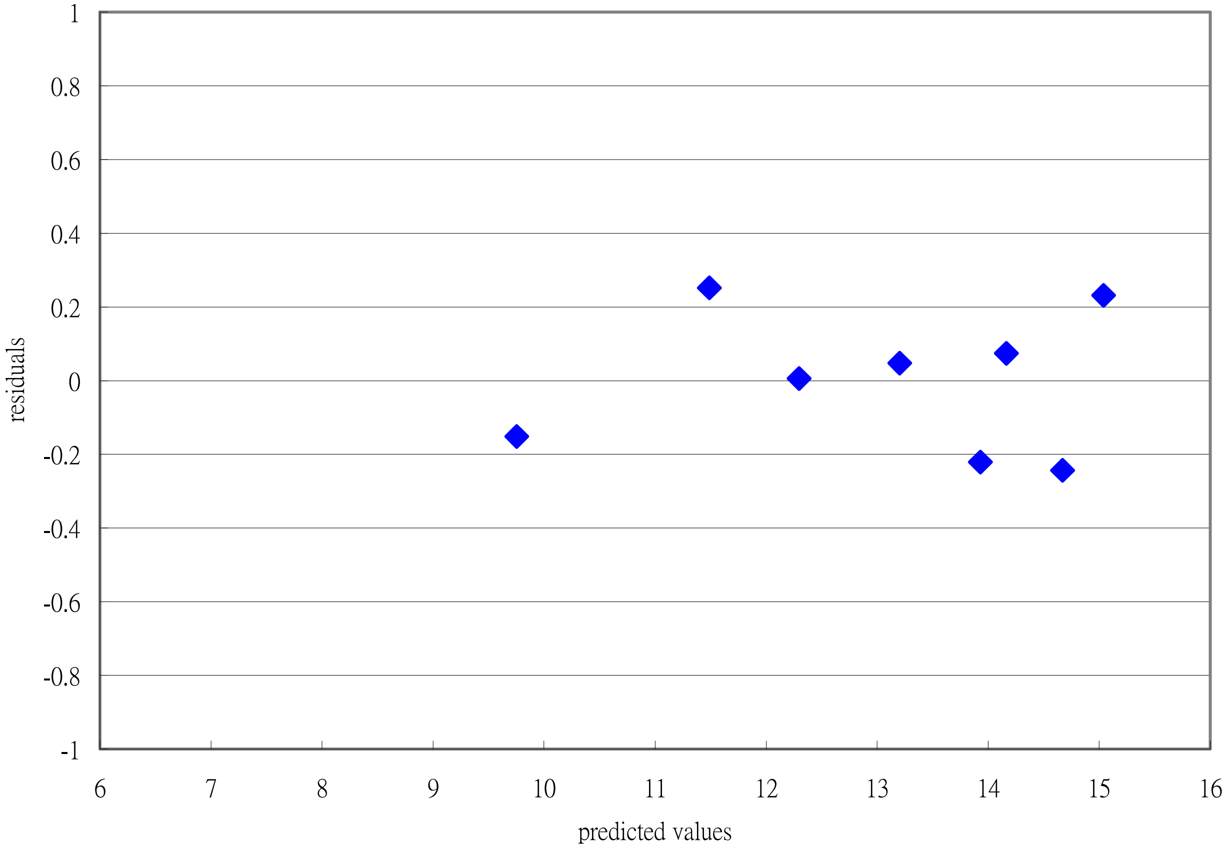
(**2a**) Freundlich equation



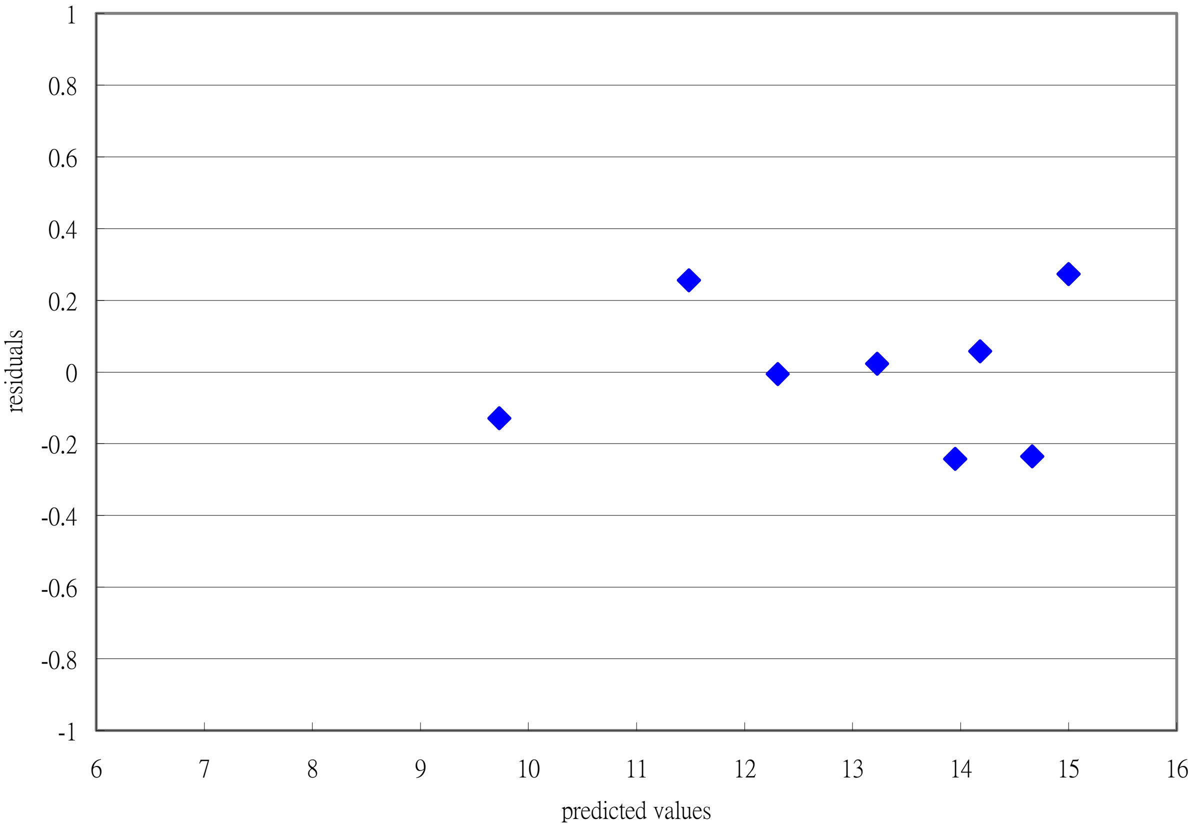
(**2b**) Langmuir equation



(**2c**) Tempkim equation



(**2d**) Redlich-Peterson equation



(**2e**) Hill equation

(**2f**) Toth equation

Fig. (2). (a-f). Residual plots of sorption isotherms for Ca by tree fern dor six isotherm equations.

With data from Ho [13] (Table **3**), the Toth equation produced the highest R^2 value and lowest s, ARE, EABS and MPSD values. However, the Hill equation produced the lowest HYBRID value. The equations produced inconsistent results for error functions, but residual plots revealed a uniform distribution for the three-parameter equations, Redlich-Peterson, Hill and Toth equations.

For the Wang and Qin data [14] (Table **3**), the Toth equation produced the highest R^2 value and the Tempkim had the lowest s value. The Langmuir equation produced the lowest ARE, HYBRID, EABS and MPSD values. Residual plots revealed a clean pattern for only the Freundlich equation and a uniform distribution for the other five equations.

3.3. Sorption Data for Three Metal Ions

The isotherm constants and error functions for three metal ions from Mckay and Portor [7] are listed in Table **4**.

For the Cu ion, the Hill equation produced the highest R^2 value and the lowest EABS value. The Toth equation had the lowest HYBRID and MPSD values. The Redlich-Peterson equation produced lowest ARE value. The experimental data and predictive curves for the six equations are shown in Fig. (**3**) and the residual plots are presented in Fig. (**4**). Residual plots showed a clean pattern for the Freundlich and Langmuir equation and a uniform distribution for the Tempkim, Redlich-Peterson, Hill and Toth equation.

For the Cd ion, the Hill equation produced the highest R^2 value and the lowest s, ARE, HYBRID, EABS and MPSD values. Residual plots showed a clean pattern for the two-parameter equations, Freundlich, Langmuir and Tempkim equations, and a uniform distribution for the three-parameter equations, Redlich-Peterson, Hill and Toth. For experimental datasets, the Hill equation could be the best equation to describe the relationship between adsorbate and adsorbent concentrations.

For the Zn ion, the Toth equation produced the highest R^2 value and the Hill equation had the lowest EABS value. The Langmuir equation produced the lowest s, ARE, HYBRID and MPSD values. Residual plots showed the uniform distribution for four equations except the Freundlich and Tempkim equations.

3.4. Effect of Temperature on Isotherm Data

The data for ammonium biosorption by *Posidonia oceanica* seagrass fibers at five temperatures were from Wahab et al. [4]. The estimated constants and error functions are listed in Table **5**. Residual plots showed the clean patterns for the Freundlich and Tempkim equation and the uniform distribution for other four equations (Fig. **5**). However, the error functions showed inconsistent results.

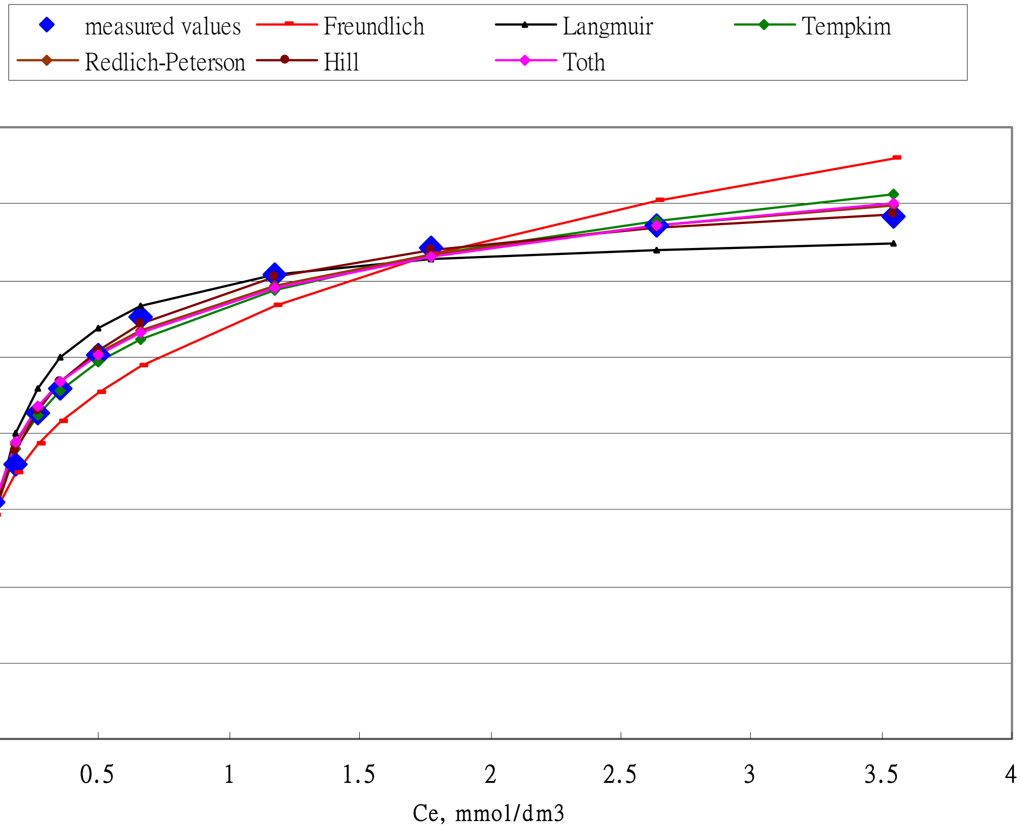
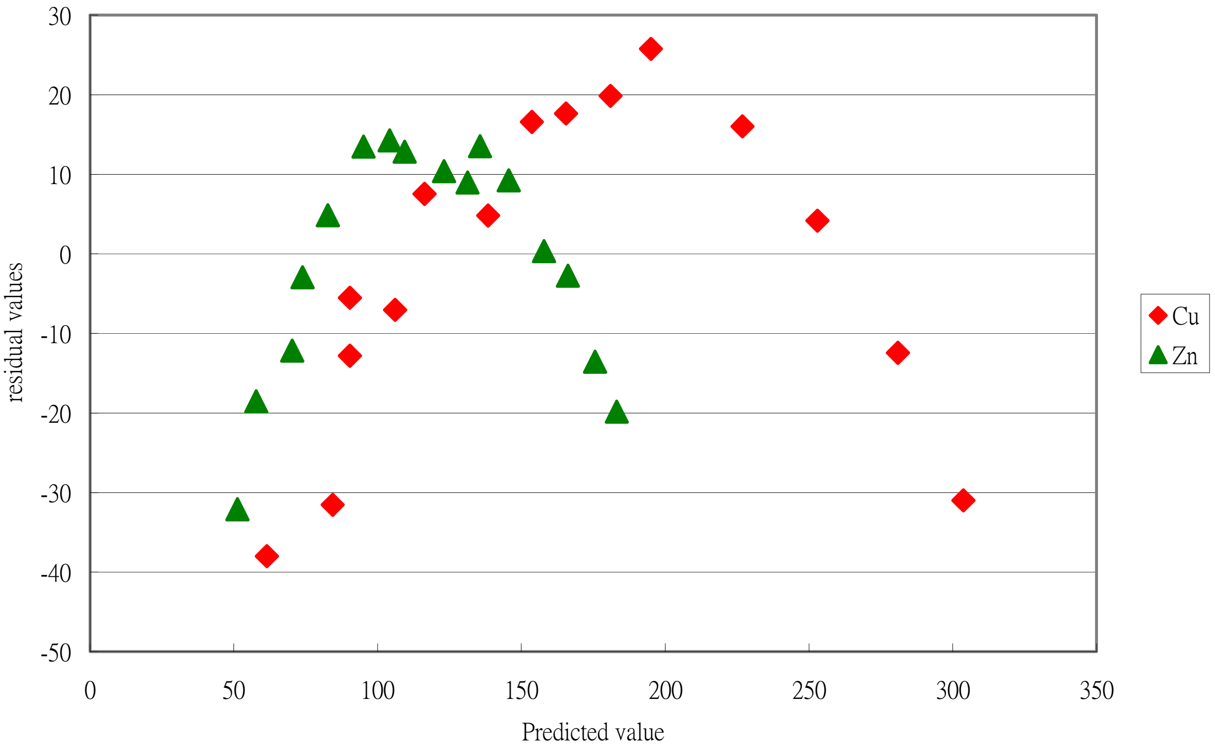
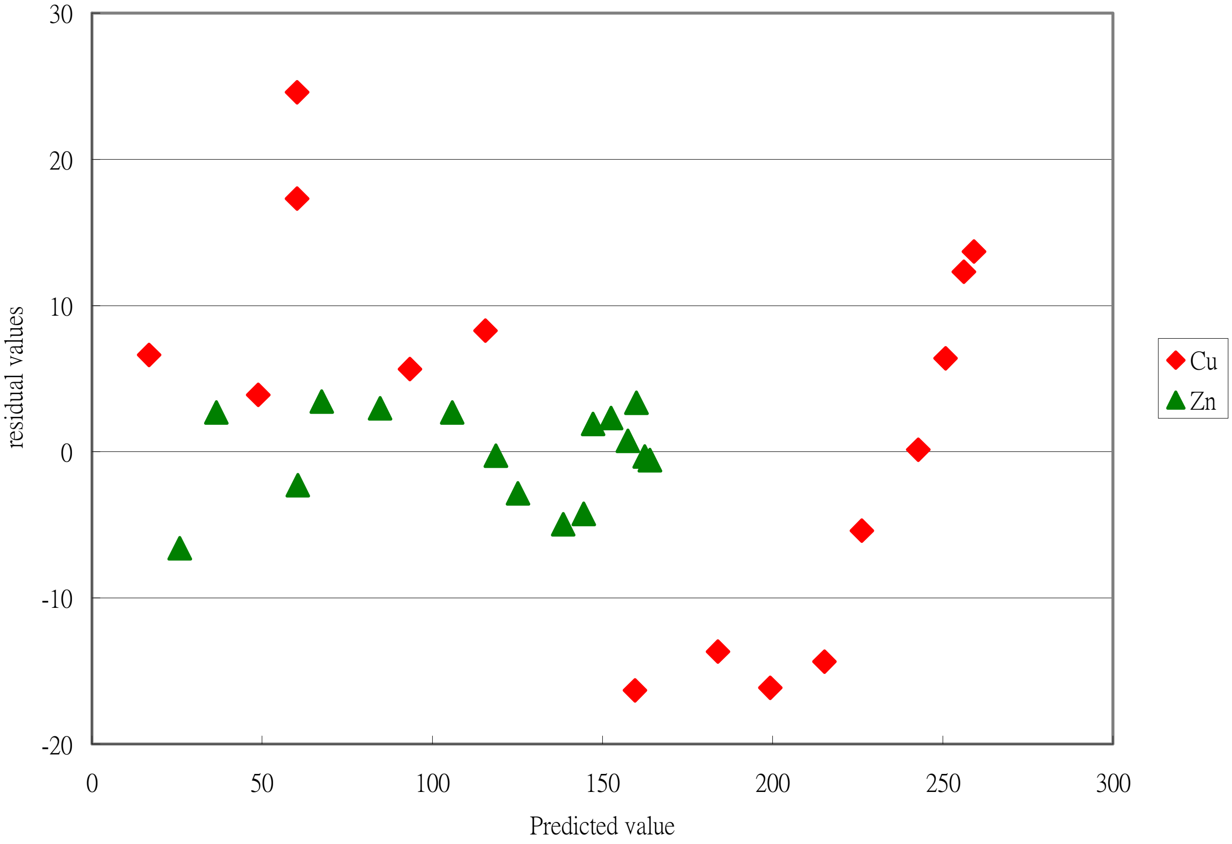


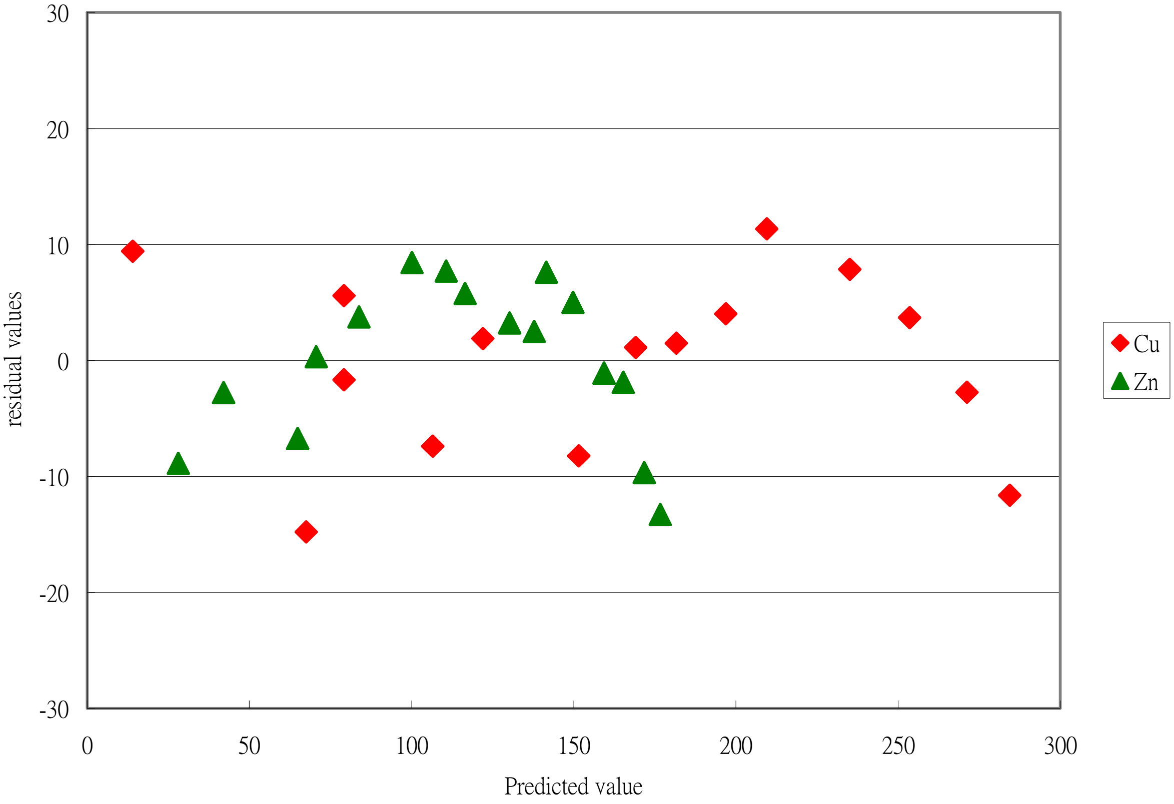
Fig. (3). Sorption isotherms for Cu by peat for six isotherm equations.



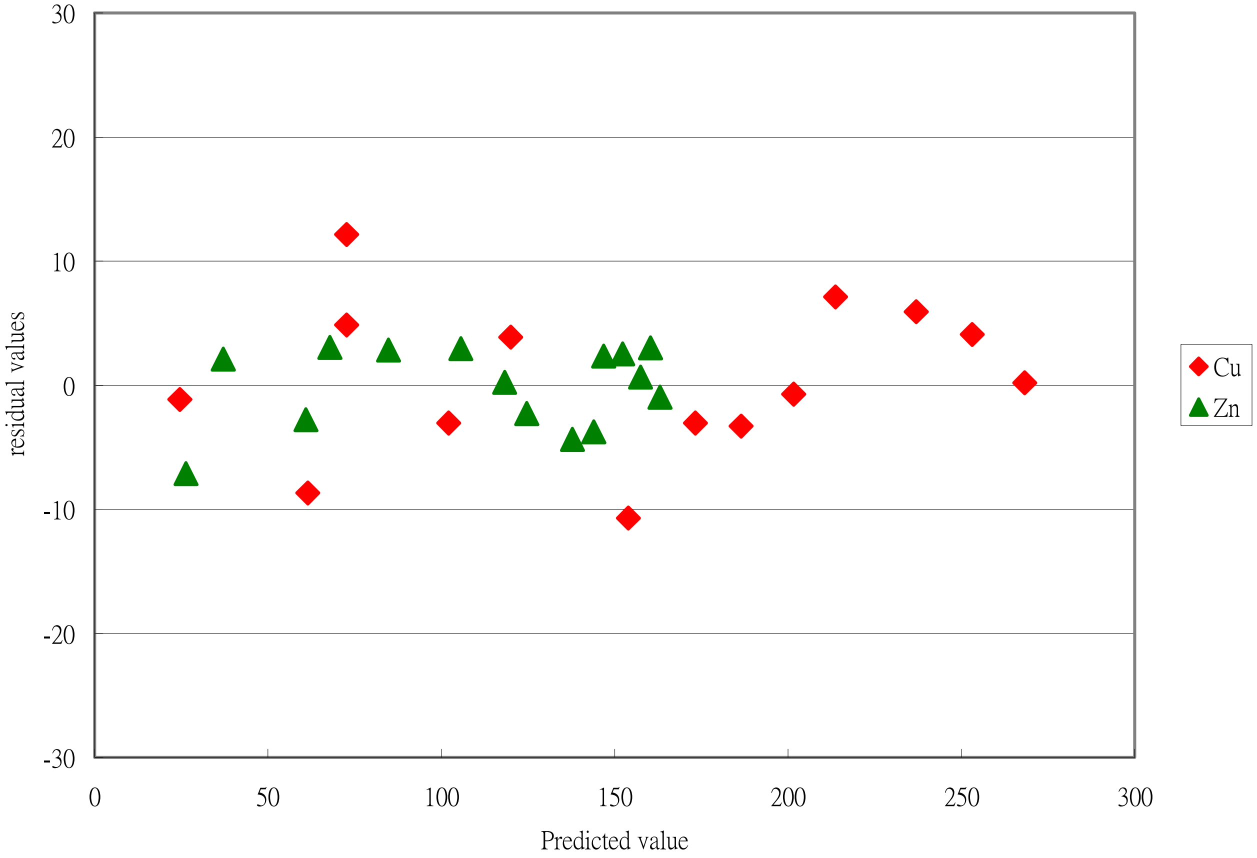
(**4a**) Freundlich equation



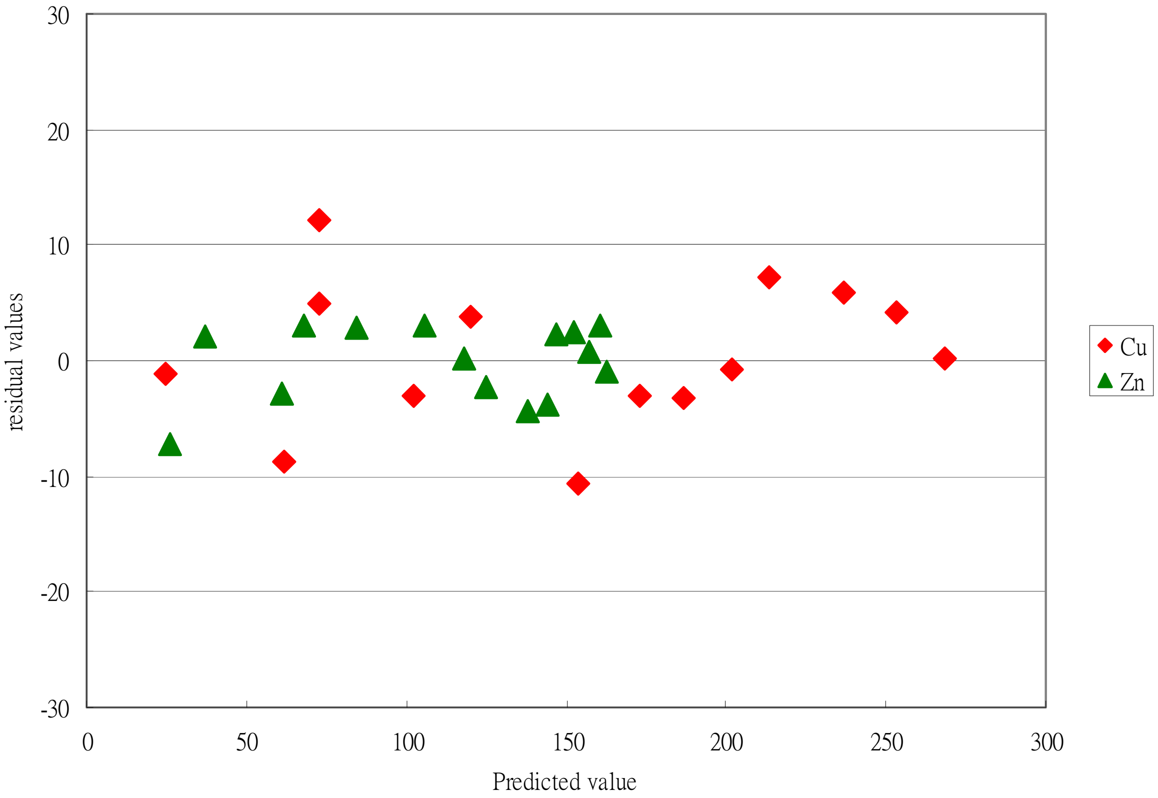
(**4b**) Langmuir equation



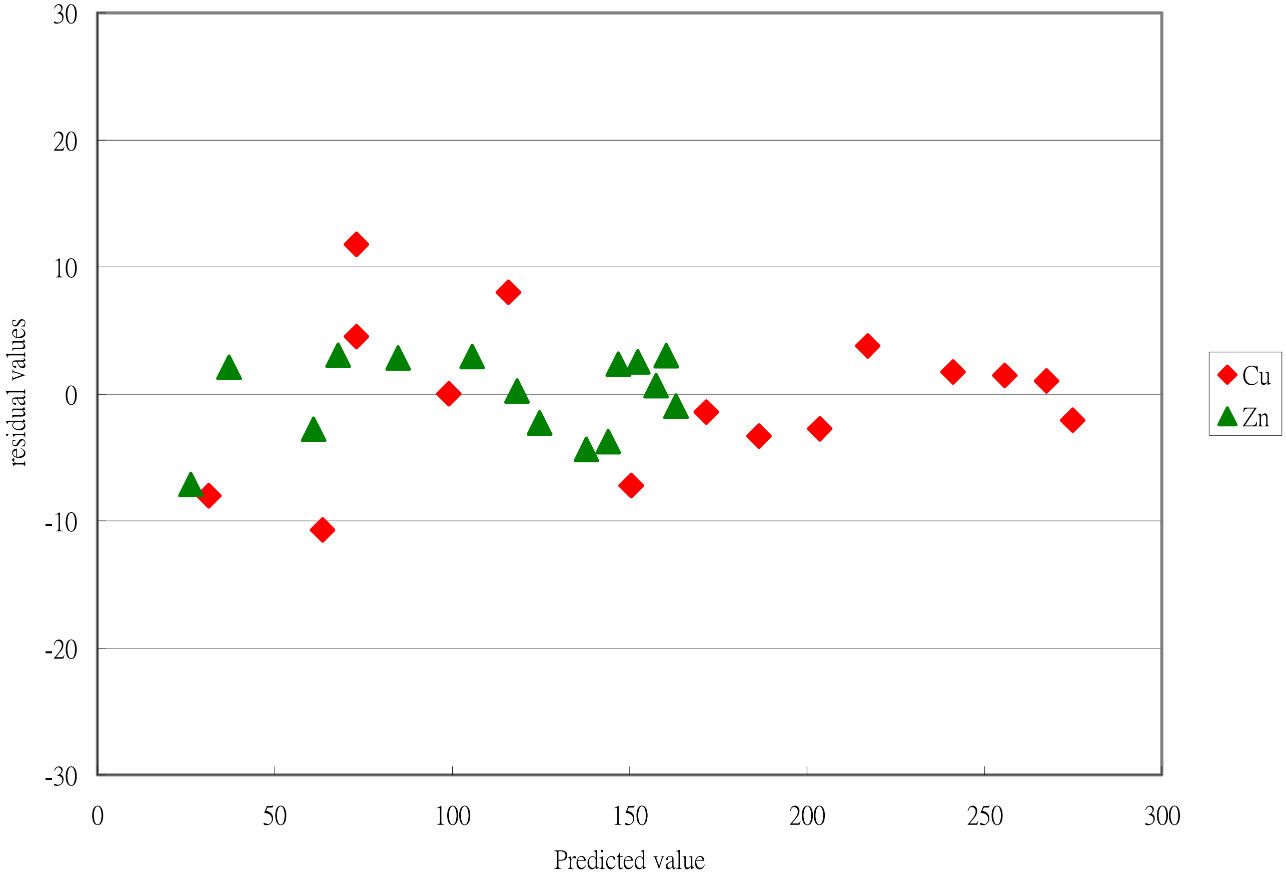
(**4c**) Tempkim equation



(**4d**) Redlich-Peterson equation

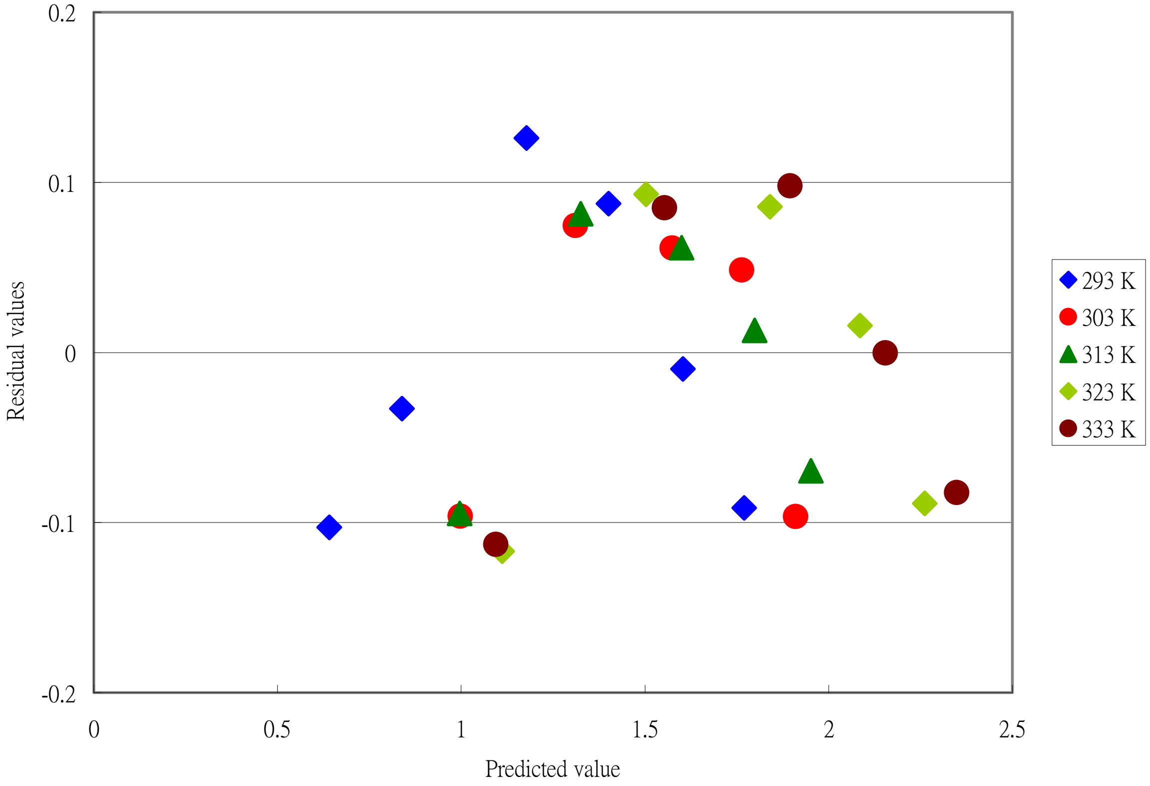


(**4e**) Hill equation

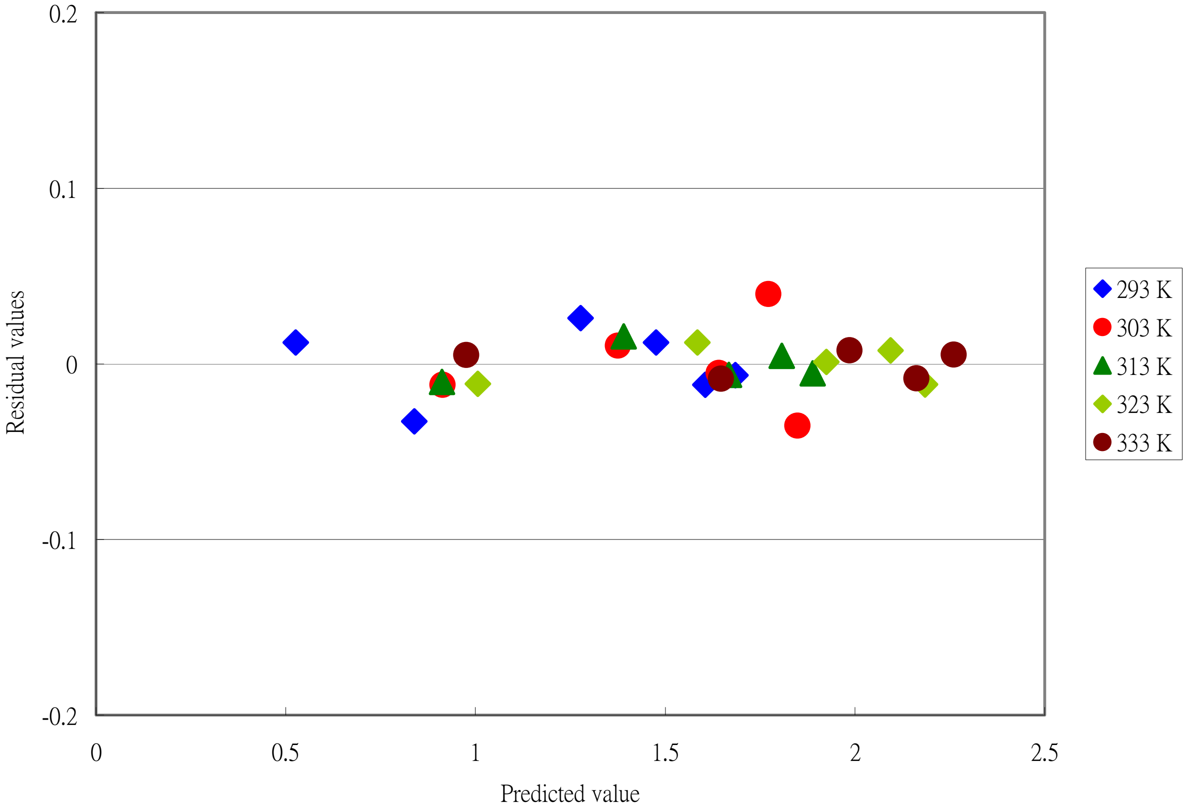


(**4f**) Toth equation

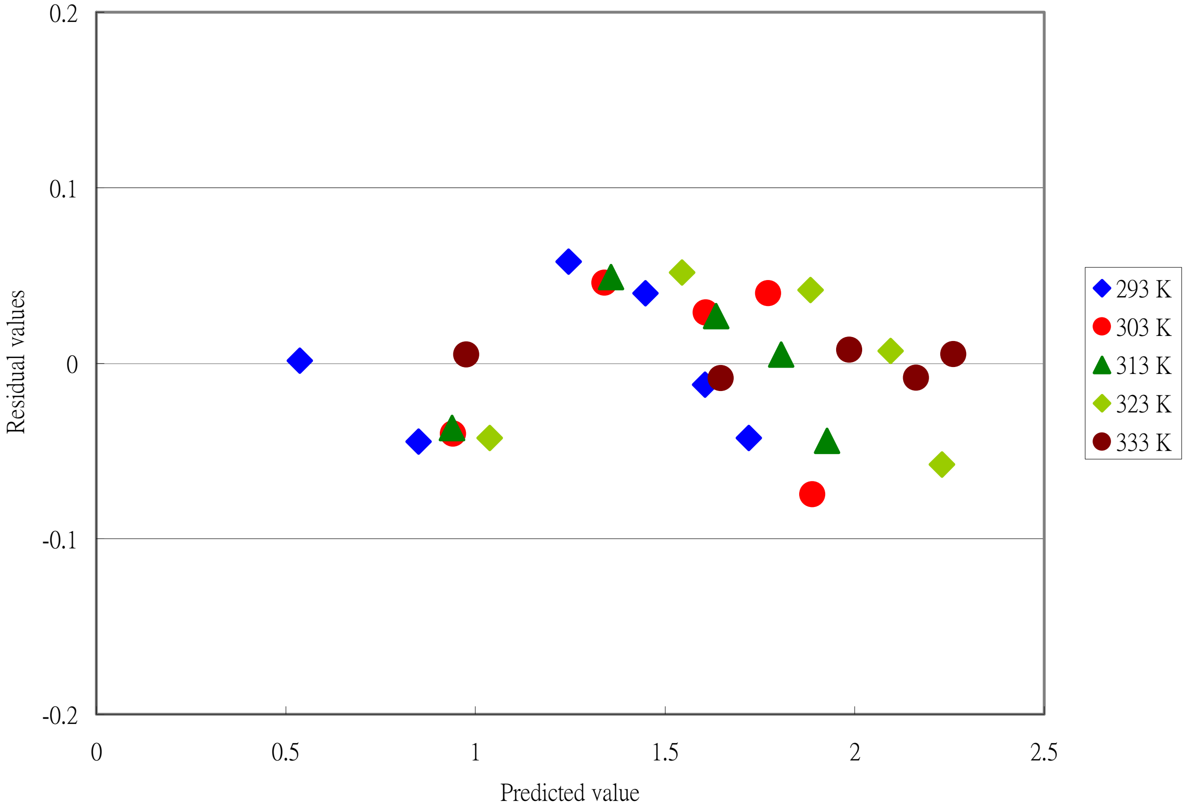
Fig. (4).(a-f) Residual plots of sorption isotherms for Cu by peat for six isotherm equations.



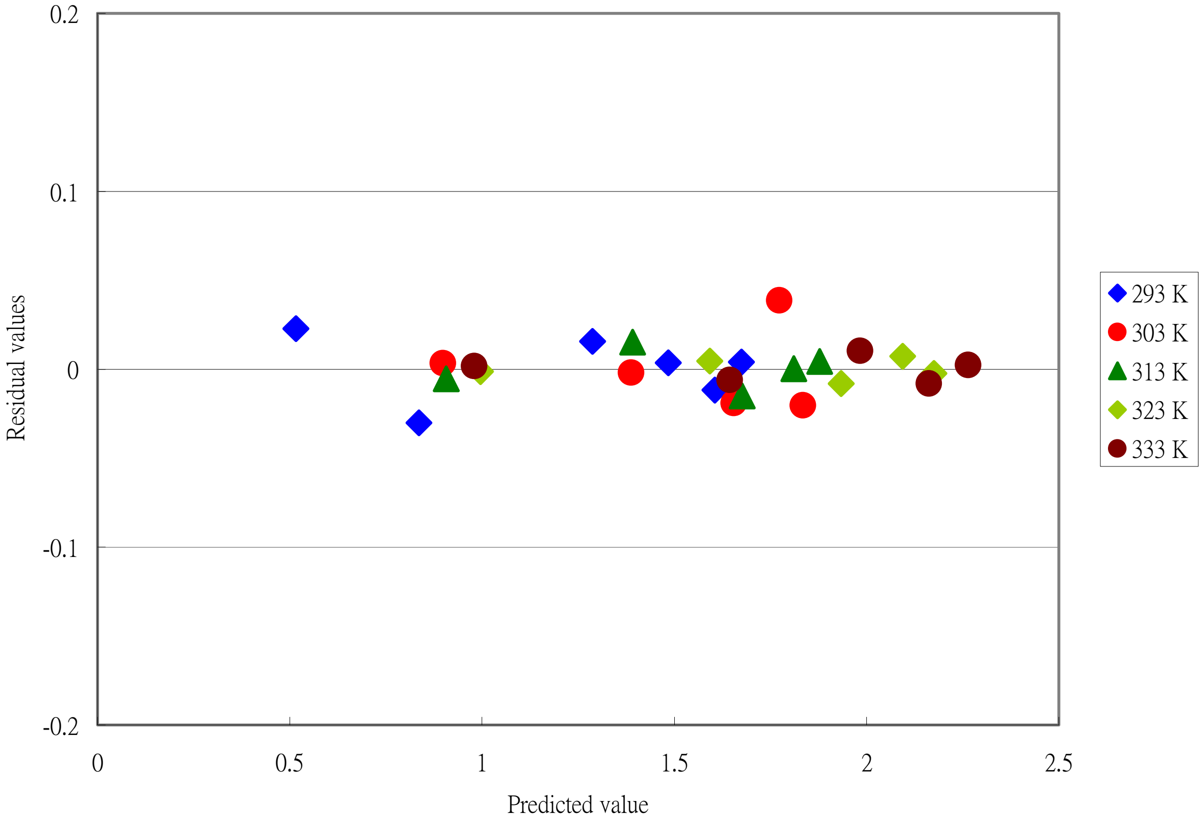
(**5a**) Freundlich equation



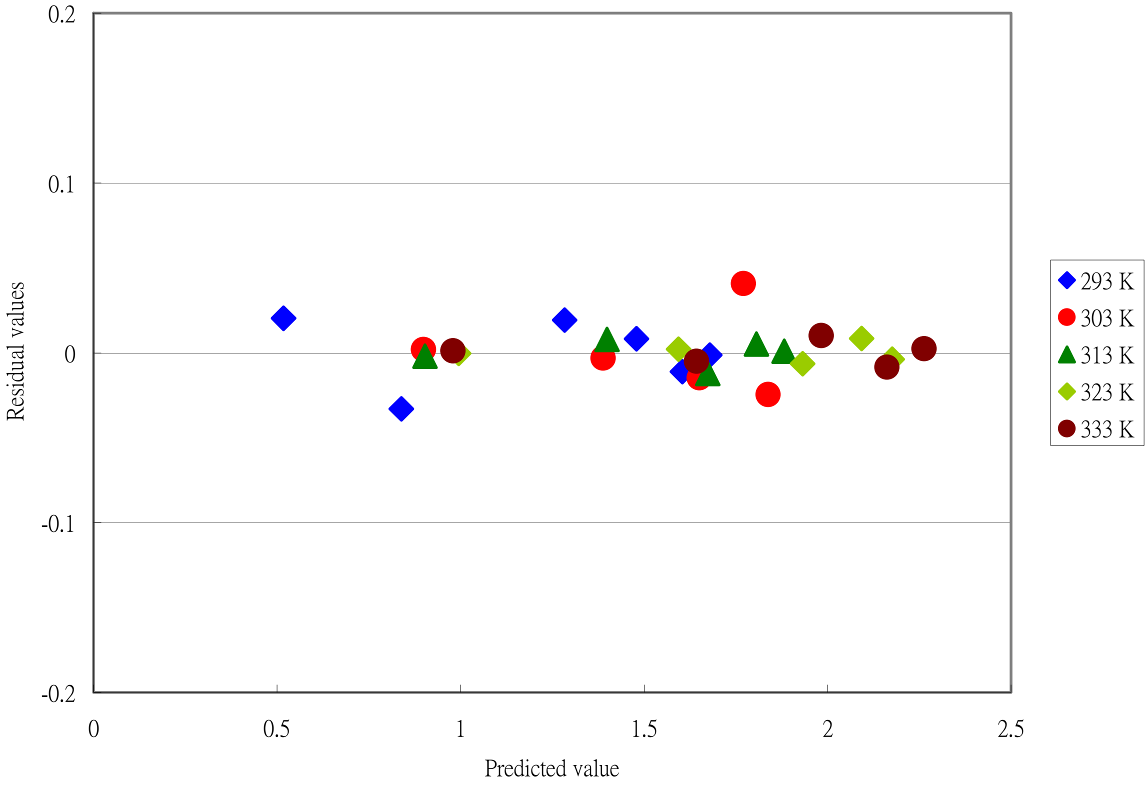
(**5b**) Langmuir equation



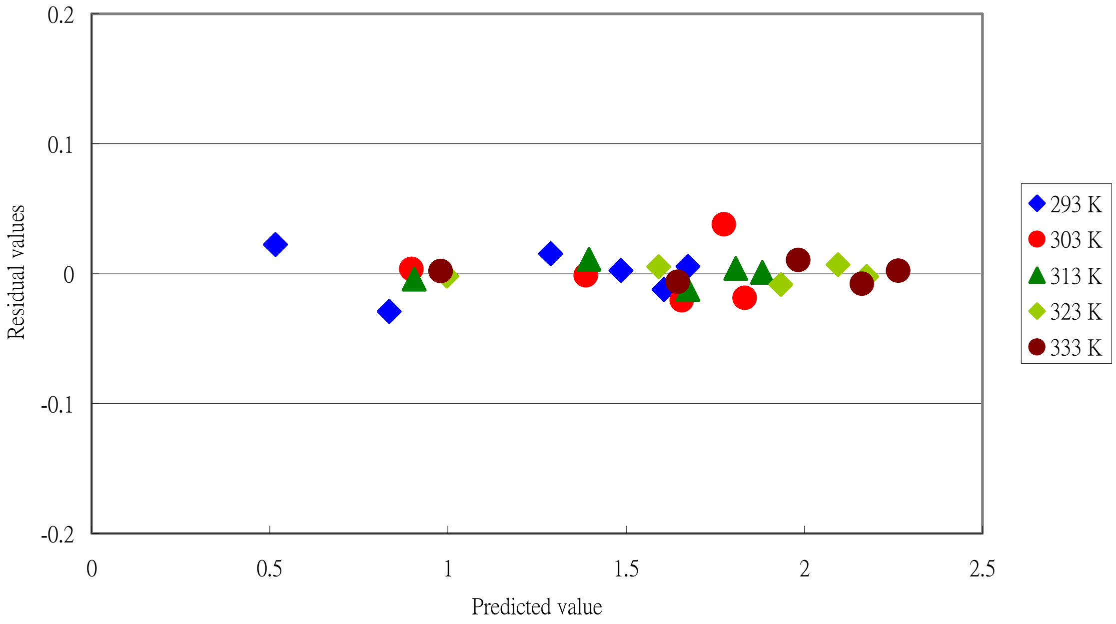
(**5c**) Tempkim equation



(**5d**) Redlich-Peterson equation



(**5e**) Hill equation



(**5f**) Toth equation

Fig. (5).(a-f) Residual plots of sorption isotherms for ammonium by *Posidonia Oceanica* seagrass fibers at five temperatures using six isotherm equations.

Table 4. Isotherm Constants and Error Functions for Six Isotherm Equations with Data for Three Metal Ions from Mckay and Porter [7]

Metal ion		Freundlich	Langmuir	Tempkim	Redlich Peterson	Hill	Toth
Cu							
	A	217.7535	267.9622	228.098	246.2622	313.4119	239.6120
	B	0.2628	0.1213	44.4797	0.8826	0.6841	0.8669
	C				6.06704	0.3333	0.0484
	R^2	0.9388	0.9747	0.9912	0.9941	*0.9947*	0.9936
	s	21.1158	13.5671	8.0094	6.8069	6.4430	7.0975
	ARE	21.7823	11.4839	7.3508	4.6260	6.2507	4.3841
	HYBRID	25.1335	13.2506	8.4817	8.3268	7.8133	5.0585
	EABS	250.6866	164.7886	92.8681	75.6685	64.7468	77.6173
	MPSD	15.4286	14.2725	14.1529	7.3371	12.5175	7.1550
	Residual plots	CP	CP	UD	UD	UD	UD
Cd							
	A	14.5924	18.3504	15.2445	16.705	20.5359	16.4531
	B	0.2331	0.1322	2.7837	0.9079	0.6944	0.8993
	C				0.07409	0.2992	0.06110
	R^2	0.9318	0.9782	0.9798	0.9878	*0.9942*	0.9864
	s	1.4358	0.8116	0.7811	0.6308	0.4331	0.6659
	ARE	16.5813	10.2970	7.9223	6.4250	3.4502	6.9750
	HYBRID	19.9501	11.6994	9.0541	7.3429	3.9431	7.9714
	EABS	19.0611	9.4692	10.3336	7.1991	4.5551	7.6083

Table 4 Contd…..

MPSD	32.8337	20.2178	13.4104	12.9911	5.6228	14.2451
Residual plots	CP	CP	CP	UD	UD	UD
Zn						
A	131.7768	174.3585	138.1973	172.478	174.4824	170.8452
B	0.2824	0.2038	32.9692	0.9876	0.9979	0.9819
C				0.1951	0.2049	0.1883
R^2	0.9059	0.9953	0.9796	0.9954	0.9953	*0.9955*
s	14.9880	3.3405	6.9862	3.4217	3.4664	3.4096
ARE	20.7031	4.4387	7.3058	4.5284	4.4495	4.5250
HYBRID	23.6610	5.0728	8.3495	5.5734	5.4763	5.5692
EABS	189.7629	42.2543	88.5656	42.4924	42.2351	42.5986
MPSD	47.3633	9.7111	13.6319	10.7227	10.1558	10.7037
Residual plots	CP	UD	CP	UD	UD	UD

Table 5. Isotherm Constants and Error Functions for Six Isotherm Equations with Data for Five Temperatures from Wahab et al. [4])

Temperature	Freundlich	Langmuir	Tempkim	Redlich- Peterson	Hill	Toth
293 K						
A	0.4156	2.0278	0.03130	2.4254	1.9818	2.9056
B	0.3844	8.8140	0.4484	1.0458	1.0431	1.0819
C				10.1947	8.4264	10.9211
R^2	0.9590	0.9979	0.9917	*0.9983*	0.9981	*0.9983*
s	0.1044	002360.0236	0.04710.0471	0.0247	0.0262	0.0243
ARE	7.4650	1.7105	2.7028	1.6887	1.7802	1.7017
HYBRID	11.1975	2.5658	4.0543	3.3773	3.5603	3.4034
EABS	0.4503	0.10135	0.1984	0.08376	0.09321	0.08707
MPSD	11.6114	2.5933	4.0143	3.3566	3.3690	3.2914
Residual plots	CP	UD	CP	UD	UD	UD
303K						
a	0.5952	2.1762	0.1888	2.8471	2.0784	3.5950
b	0.316	7.0813	0.4607	1.0690	1.1222	1.1160
c				10.5057	8.2129	9.8610
R^2	0.9484	0.9947	0.9801	0.9961	0.9957	*0.9962*
s	0.1004	0.0321	0.0625	0.338	0.0353	0.0333
ARE	5.5600	1.3038	3.1700	0.9868	0.9882	0.9750
HYBRID	9.2667	2.1730	5.2833	2.4670	2.4705	2.4375
EABS	0.3771	0.1023	0.2296	0.08342	0.08505	0.0821
MPSD	8.0083	1.9140	4.3205	1.9157	1.9736	1.8947

Table 5 Contd…..

	Residual plots	CP	UD	CP	UD	UD	UD
313K							
	a	0.5818	2.2453	0.1485	3.5253	2.1798	2.7044
	b	0.3290	7.4926	0.4834	1.0301	1.0698	1.0432
	c				8.9503	8.1110	8.5384
	R^2	0.9614	0.9993	0.9898	0.9995	*0.9996*	0.9995
	s	0.0902	0.2121	0.0464	0.0121	0.0109	0.0124
	ARE	4.884	0.6356	2.3628	0.4352	0.3691	0.4536
	HYBRID	8.140	1.0593	3.9380	1.0881	0.9227	1.1340
	EABS	0.3203	0.04227	0.1620	0.03159	0.02808	0.4843
	MPSD	5.8626	0.9730	3.5128	0.8124	0.6982	0.7156
	Residual plots	CP	UD	CP	UD	UD	UD
323K							
	A	0.6738	2.5922	0.1964	2.9908	2.5132	3.3050
	B	0.3329	7.0919	0.5592	1.0372	1.0727	1.0570
	C				8.7508	7.6557	8.3961
	R^2	0.9592	0.9995	0.9896	0.9998	*0.9999*	0.9998
	s	0.1122	0.0126	0.0566	0.0085	0.0082	0.0088
	ARE	5.3720	0.5745	2.5364	0.2597	0.2190	0.2758
	HYBRID	8.9533	9.5743	4.2273	6.493	5.4760	0.6895
	EABS	0.4001	0.04410	0.2008	0.02366	0.02144	0.02452
	MPSD	8.3467	0.8813	0.6847	0.4506	0.40632	0.4749
	Residual plots	CP	UD	CP	UD	UD	UD
333 K							
	A	0.6744	2.6931	0.1892	2.5833	2.7253	2.5250
	B	0.3442	7.1712	0.5846	0.9892	0.9778	0.9847
	C				6.7386	6.7327	6.8280
	R^2	0.9662	*0.9998*	0.9943	*0.9998*	*0.9998*	*0.9998*
	s	0.1101	0.0091	0.0453	0.0104	0.0102	0.0104
	ARE	5.0516	0.4022	1.9404	0.3053	0.2842	0.3126
	HYBRID	8.4193	0.6703	3.2340	0.7634	0.7104	0.7815
	EABS	0.3786	0.0344	0.1612	0.02829	0.02706	0.02871
	MPSD	8.0953	0.5363	2.7556	0.5385	0.5148	0.5473
	Residual plots	CP	UD	CP	UD	UD	UD

For the 293 K temperature data, the Redlich-Peterson and Toth equation produced the same R^2 values. The Toth equation had the lowest s value and the Redlich-Peterson equation had the lowest ARE and EABS values. The Langmuir equation had the lowest HYBRID and MPSD values.

For the 303 K temperature data, the Toth equation had the highest R^2 value and lowest ARE, EABS and MPSD values and the Langmuir equation had the lowest s and HYBRID values.

For the 313 K temperature data, the Hill equation could be the best fitting ability, it had the highest R^2 value and lowest value for other criteria.

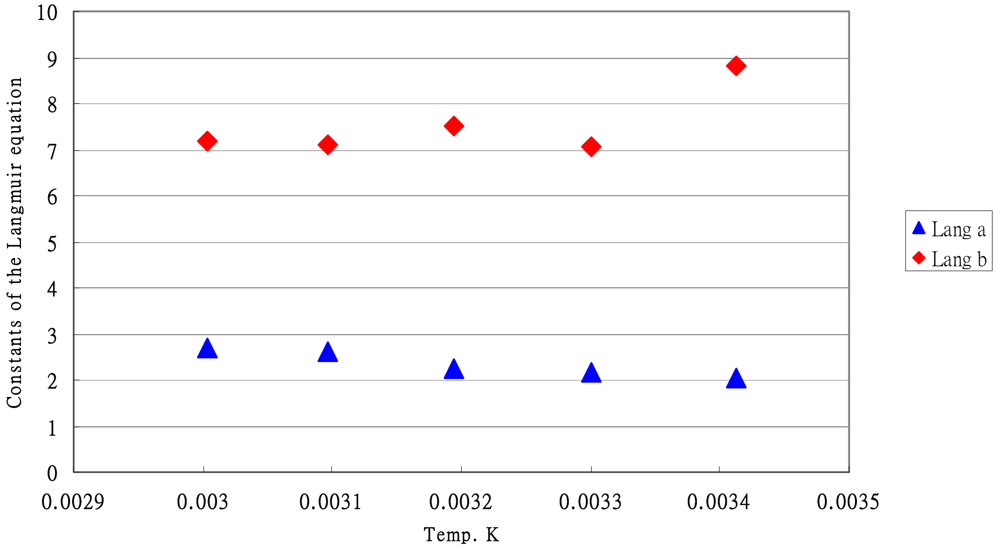
For the 323 K and 333 K temperature data, results for error functions were inconsistent.

The isotherm constants of Langmuir and Hill equations were used to study the effect of temperature on sorption isotherms (Fig. **6**). Temperature was significantly associated with k_L and a_L of the Langmuir equation and q_{SH} and k_D but not nH of the Hill equation.

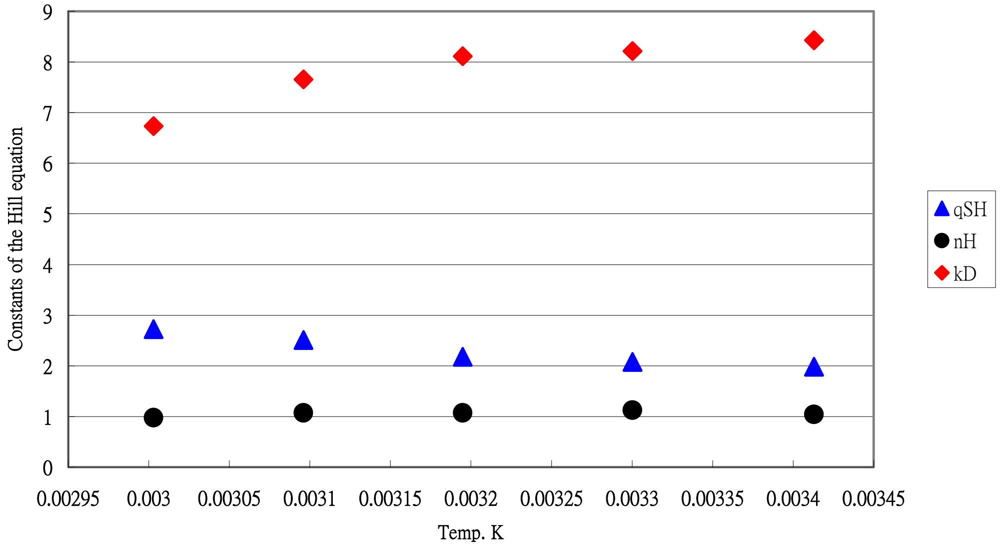
In the study of the sorption isotherm for metal ions on tree fern, the experiments were tested at four temperatures [6]. Temperature was significantly associated with k_L and $a_L$of the Langmuir isotherm were listed. The results were similar as this study.

Many sorption isotherm equations are nonlinear equations. Linearization methods had been adopted to transform dependent and independent variables for linear regression analysis. The problems have been reviewed [16].

The Langmuir isotherm equation was used to demonstrate the expanded variance of constants with linearization [23]. EI-Khaiary *et al*. [17] analyzed simulated data by nonlinear regression and four linearized forms of the pseudo-second-order equation. Nonlinear regression had the minimum variance and was considered the most accurate methods. The current study compared three two-parameter and other three three-parameter isotherm equations analyzed with the nonlinear regression analysis. Six error functions were



(**6a**) Langmuir equation



(**6b**) Hill equation

Fig. (6).(a-b) Effect of temperature on constants of two isotherm equations.

selected to compare the fitting-agreement of isotherm equations. The inconsistent results were found. Only the Hill equation produced the lowest values for all error functions for Cd ions. For most data, no isotherm equation produced all the low values for errors functions. Similar results can be found in the literatures. Five isotherm equations were selected to study adsorption of two basic dyes by kudzu [11], the linear-transformed Redlich-Peterson equation produced the highest R^2 value, but did not have the lowest values for the other error functions.

Seven isotherm equations were tested for toxin adsorption with yeast biomass [8]. For OA adsorption by EX16 yeast biomass, the Hill equation produced the lowest values for the six error functions. For OA adsorption by beta-glucanes, the Hill equation had the lowest MPSD, ARE and the sum of normalized errors (SNE). However, the Toth equation produced the lowest HYBRID and EABS values and the BET equation had the lowest sum of the squares of errors (ERRSQ). Inconsistent results were found for OA adsorption by a yeast cell wall fraction (LEC).

A new error function, the small-sample-corrected Akaike information criterion (AICc) was proposed to evaluate seven isotherm equations [15]. The Freundlich equation best described the adsorption of Cu^{2+} and Cd^{2+} data by Bentonite adsorbents. However, the HYBRD, ARE, MPSD and EABS values for the Freundlich equation were higher than for other isotherm equation such as Langmuir, Redlich-Peterson and Sip.

Results were inconsistent in evaluating the predictive ability of isotherm equations for adsorption of textile dye by *Posidonia oceanica* seagrass fibres [22]. The Redlich-Peterson equation had highest R^2 value and the lowest ARE, MPSD, HYBRID, ERRSQ and s values. However, this equation had the highest values by Students *t* test.

Researchers have plotted the data distribution of the amount of ion sorbed (q_e) versus the isotherm equilibrium concentration (C_e) and the predictive curves of several isotherm equations were used by researchers [2,6,8,12-14,18]. However, the fitting ability is not easily justified visually. In this study, residual plots were dfound to be an adequate quantitative evaluation method. As the model is inadequate, the predictive values were under-or over-estimated. The inadequate results are easy to observe with the data distribution of residual plots.

The effect of the temperature on sorption isotherms has been analyzed [4-6,24]. In this study, with data from Wahab *et al.* [4] , temperature was associated with constants of the Langmuir equation and two constants of the Hill equation. The effect of the temperature on constants could be expressed as a temperature function and then incorporated into isotherm equations to express the relationship among C_e, q_e, and temperature. The development and validations of an adequate isotherm equations incorporating a temperature term remains for further studied.

CONCULSION

This study used eleven datasets from the literatures to assess the fitting ability of sorption isotherm equations in determining the capacity of an adsorption system to treat industrial wastewater. Nonlinear regression analysis was used to avoid problems with linearization which alters the error distribution and distorts the variance structure. Results for error functions were inconsistent among sorption isotherms, but residual plots were useful to observe the fitting ability of isotherm equations. Temperature had a significant effect on the constants of isotherms. Incorporating a temperature term into isotherm equations needs further study.

CONFLICT OF INTEREST

The author has none to declare.

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