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Research Article

Isotherm Study of Phosphorus Uptake from Aqueous Solution Using Aluminum Oxide

Aluminum oxide, which could be an alternative filter media for phosphorus uptake from aqueous solution, was selected as an adsorbent for the isotherm study of phosphorus uptake from aqueous solution. Batch method was adopted to investigate the adsorption behavior of phosphorus onto aluminum oxide. The Langmuir, Freundlich, and Redlich–Peterson isotherms were used to analyze the experimental data by both the linear and nonlinear regression methods. The adsorption experiment was conducted at various temperatures, to choose the appropriate method and obtain the creditable adsorption parameters for phosphorus uptake studies. The results indicated that the nonlinear regression method might be a better way to compare the best-fitting isotherm and obtain the parameters for the adsorption of phosphorus onto aluminum oxide. Both the Redlich–Peterson and the Freundlich isotherms have high coefficients of determination for the adsorption of phosphorus onto aluminum oxide at various temperatures. In addition, a new relationship between the Redlich–Peterson and the Freundlich isotherm parameters was presented.

Keywords: Adsorption; Aluminum oxide; Isotherm parameters; Nonlinear regression; Phosphorus

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1 Introduction

Phosphorus is considered to be the significant nutrient causing water pollution. Phosphorus removal mechanism from aqueous solution includes adsorption, desorption, precipitation, leaching, uptake, fragmentation, mineralization, sedimentation, and burial [1, 2]. Adsorption equilibrium studies are always conducted to help researchers investigate the adsorption characteristic and capacity of phosphorus onto filter medium [3, 4]. The previous adsorption equilibrium studies are usually based on linear regression method, but it has also been presented that using this linear regression method for comparing the best-fitting isotherms is not appropriate [5]. The adsorption behaviors by using aluminum oxide (Al_2O_3) as adsorbents in various solvents have been earlier studied for several decades [6, 7]. In recent years, Bushey and Dzombak [8] used aluminum oxide as an adsorbent for removal of ferrocyanide from aqueous solution and found that ferrocyanide could be adsorbed by aluminum oxides significantly. A batch method was also employed to study the adsorption behavior of Cr(VI) from synthetic solutions on aluminum oxide, and the Langmuir isotherm was found to describe the adsorption process well [9].

In this study, Al_2O_3, which could be an alternative filter media for phosphorus uptake from aqueous solution, was selected as an adsorbent to investigate its adsorption characteristic of phosphorus. The Langmuir, Freundlich, and Redlich–Peterson isotherms were used by the linear and nonlinear regression methods. The aims of this study were to compare these two regression methods, choose the appropriate method, and then obtain the creditable adsorption parameters for Al_2O_3 adsorption equilibrium studies.

2 Materials and Methods

A commercial Al_2O_3 powder, available in Nanjing, Jiangsu Province, People's Republic of China, was applied in this study. It was analyzed for particle size distribution by using laser diffraction particle size analyzer, Malvern ZetaSizer 3000. The X-ray fluorescence spectrometer, Bruker AXS S4 Pioneer was used for the composition analysis.

A synthetic phosphorus solution comprising distilled water and potassium dihydrogen phosphate was used. The concentrations of solutions were calculated as phosphorus subsequently and the phosphates hereinafter collectively referred to as the "phosphorus." A stock solution of 500 mg/dm^3 was prepared by dissolving a weighed amount of phosphorus in 1000 mL of distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary. A phosphorus solution of 50 mL with a concentration ranging from 10 to 150 mg/dm^3 was placed into several 150 mL conical flasks. A weighed amount (0.1 g) of the Al_2O_3 was added to the solution. The conical flasks were then shaken at a constant speed of 170 rpm in a shaking water bath at temperatures of 283, 293, 298, 303, and 308 K, respectively. After shaking the flasks for 12 h, the Al_2O_3 powders were separated by centrifugation. The phosphorus solution was analyzed for the remaining phosphorus concentration with ammonium molybdate spectrophotometric method by a spectrophotometer. The amount of

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phosphorus adsorbed onto Al_2O_3 was calculated by using the following expression:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e was the equilibrium adsorption capacity of phosphorus adsorbed on unit mass of the Al_2O_3 (mg/g); C_0 was the initial phosphorus concentration (mg/dm^3); C_e was the phosphorus concentration at equilibrium (mg/dm^3); V was the volume of the phosphorus solution (dm^3); and m was the weight of Al_2O_3 (g).

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. In order to investigate the adsorption isotherm, three equilibrium isotherms were analyzed: the Langmuir, Freundlich, and Redlich–Peterson, respectively.

The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption [10]. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as Eq. (2) [11]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg/g); C_e is the equilibrium liquid phase concentration (mg/dm^3); q_m is the maximum adsorption capacity (mg/g); K_a is adsorption equilibrium constant (dm^3/mg).

The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm [12]. This fairly satisfactory empirical isotherm can be used in adsorption from dilute solutions. The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where C_e is the equilibrium concentration in the solution (mg/dm^3); q_e is the equilibrium adsorption capacity (mg/g); K_F and $1/n$ are empirical constants. K_F is the adsorption value, the amount adsorbed at unit concentration, that is, at 1 mg/dm^3. It is characteristic for the adsorbent and the adsorbate adsorbed.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms [13]. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{4}$$

where q_e is the equilibrium adsorption capacity (mg/g) and C_e is the equilibrium liquid phase concentration (mg/dm^3). It has three isotherm constants, namely, A, B, and g ($0 < g < 1$).

The coefficient of determination, r^2, between the experimental data and isotherms is used to test the best-fitting isotherm [14]. The coefficient of determination r^2 is defined as:

$$r^2 = \frac{\sum (q_m - \overline{q_e})^2}{\sum (q_m - \overline{q_e})^2 + \sum (q_m - q_e)^2} \tag{5}$$

where q_m is the equilibrium capacity obtained from the isotherm (mg/g); q_e is the equilibrium capacity obtained from experiment (mg/g); and $\overline{q_e}$ is the average of q_e (mg/g).

3 Results and Discussion

3.1 Properties of Al_2O_3 Powder

The particle size distribution of Al_2O_3 was as follows: 315–405 nm (66.4%), 405–500 nm (33.6%), respectively. The average size was 395.6 nm. The result of XRF analysis is shown in Tab. 1.

Table 1. Main chemical compositions of Al_2O_3.

Composition	Percent (%)	Composition	Percent (%)
Al_2O_3	86.3	MgO	0.389
CO_2	7.93	SO_3	0.359
CaO	3.19	Na_2O	0.114
SiO_2	0.727	Fe_2O_3	0.0935
Cl	0.713		

3.2 Comparison of Linear and Nonlinear Regression Methods

Linear least-squares regression method and trial-and-error nonlinear regression method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel, both used to obtain the isotherm parameters, were discussed [14]. These two methods were used to compare the best fitting of three isotherms. The Langmuir isotherm could be linearized as four different types, while the Freundlich isotherm had two different types usually (Tab. 2) and simple linear regression would result in different parameter estimates [14–16]. The more popular linear forms used are Langmuir-1 and Freundlich-1. In order to assess different isotherms and their performance to correlate with experimental results, the theoretical plots from each isotherm are shown with the experimental data for adsorption of phosphorus onto Al_2O_3 at various temperatures. The isotherm was plotted in the form of phosphorus adsorbed per unit mass of Al_2O_3, q_e against the concentration of phosphorus remaining in solution, C_e. Figure 1 compares the Langmuir isotherms obtained by using the regression method with four linear and the nonlinear isotherms for the adsorption of phosphorus onto Al_2O_3 at a temperature of 303 K. The experimental data fitted better in case of the Langmuir-1 than other three linear results. Figure 2 shows three widely used isotherms by using the nonlinear regression method with the experimental data for the adsorption of phosphorus onto Al_2O_3 at a temperature of 303 K. Values of the coefficient of determinations, r^2, obtained by using both the linear and nonlinear regression methods, are presented in Tab. 3 for the adsorption of phosphorus onto Al_2O_3 at temperatures of 283, 293, 298, 303, and 308 K, respectively. These values of the coefficient of determinations obtained from linear Langmuir-1 were calculated to be 0.995, 0.992, 0.990, 0.993, and 0.992, respectively. The result indicated that there was strong positive evidence that the adsorption of phosphorus onto Al_2O_3 followed the Langmuir isotherm using the result of Langmuir-1 linear regression method. The Langmuir isotherm parameters obtained from various linear forms were significantly different (Tab. 3). It indicated that transformations of the nonlinear Langmuir isotherm to the linear forms implicitly altered the error structure and might also violate the error variance and normality assumptions of the standard least-squares method [5, 17]. Using different linear forms of the Langmuir equation for the linear analysis would significantly affect the calculations of Langmuir parameters. Two Freundlich linear forms were also analyzed, using the same set of experimental data, by plotting log q_e versus log C_e

Table 2. Isotherms and their linear forms.

Isotherm		Linear form	
Langmuir	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$
		Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$
		Langmuir-3	$q_e = q_m - \left(\frac{1}{K_a}\right) \frac{q_e}{C_e}$
		Langmuir-4	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$
Freundlich	$q_e = K_F C_e^{1/n}$	Freundlich-1	$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)$
		Freundlich-2	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$
Redlich–Peterson	$q_e = \frac{A C_e}{1 + B C_e^g}$		$\ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$

and ln q_e versus ln C_e, respectively. The Freundlich isotherm constants, K_F, $1/n$, and the coefficients of determination, r^2, are shown in Tab. 4. The parameters obtained by using linear regression method with Freundlich-1 and Freundlich-2 are equal, that was due to the same error structures of the linear forms of the Freundlich isotherm. Figure 3 shows that two Freundlich isotherm curves, obtained by linear regression method with Freundlich-1 and Freundlich-2, are overlapped. If just the linear form of Langmuir-1 was used for comparison, Langmuir-1 should be more suitable for the experimental data than the Freundlich isotherms because of the higher value of its coefficient of determinations (Tab. 3). In contrast, if using the linear form of other Langmuir linear forms, the Freundlich isotherms were more suitable for the experimental data than the Langmuir isotherms. This discrepancy was caused by the different error structures between linear forms of Langmuir and Freundlich isotherms. Such transformations of nonlinear isotherms to linear forms implicitly altered their error structures [5, 17]. It seems that using the linear regression method for comparing the best-fitting isotherms was not appropriate for the adsorption study of phosphorus onto Al_2O_3.

The related isotherm parameters obtained by using the nonlinear regression method is shown in Tab. 5. In the case of the Langmuir isotherm, the results from the four linear Langmuir isotherms were the same. When using the nonlinear regression method, there was no problem with transformations of nonlinear Langmuir isotherm to linear forms, because they had the same error structures. The

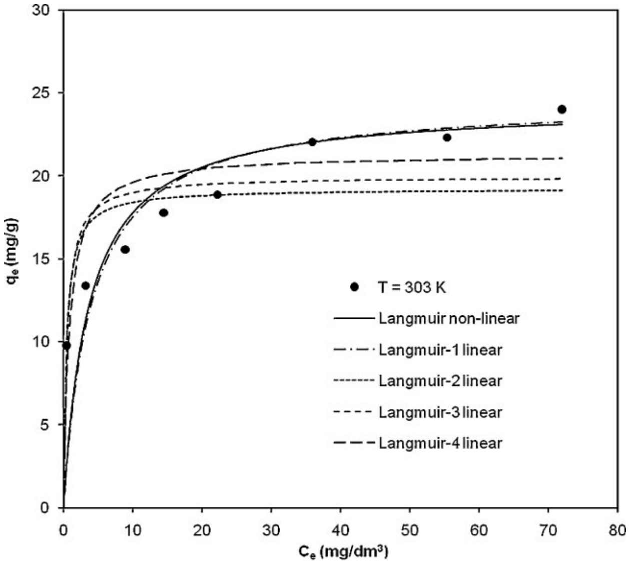

Figure 1. Langmuir isotherms obtained using linear and nonlinear regression methods for the adsorption of phosphorus onto Al_2O_3 at temperature of 303 K.

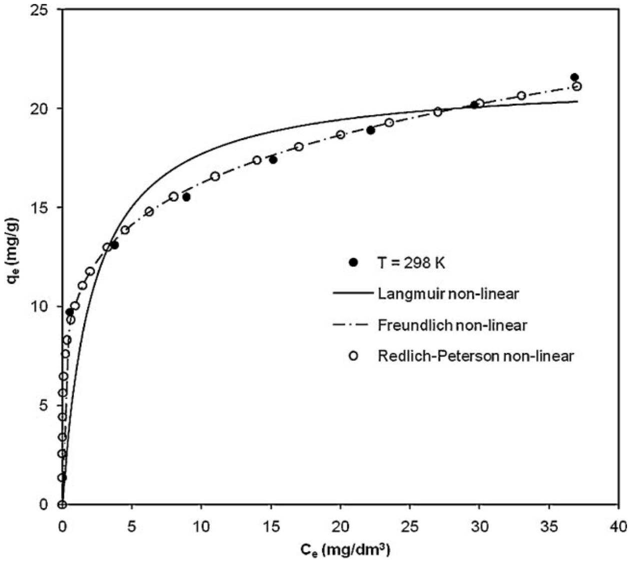

Figure 2. Isotherms obtained by using the nonlinear regression method for the adsorption of phosphorus onto Al_2O_3 at a temperature of 298 K.

Table 3. Coefficients of determination obtained by using the linear and nonlinear regression methods.

Method	T (K)	283	293	298	303	308
Linear	Langmuir-1	0.995	0.992	0.990	0.993	0.992
	Langmuir-2	0.852	0.861	0.837	0.799	0.763
	Langmuir-3	0.667	0.731	0.677	0.600	0.620
	Langmuir-4	0.667	0.731	0.677	0.600	0.620
	Freundlich-1	0.990	0.996	0.991	0.990	0.988
	Freundlich-2	0.990	0.996	0.991	0.990	0.988
	Redlich–Peterson	0.999	1.000	1.000	1.000	1.000
Nonlinear	Langmuir	0.890	0.888	0.845	0.845	0.817
	Freundlich	0.985	0.996	0.992	0.988	0.990
	Redlich–Peterson	0.986	0.996	0.992	0.988	0.990

Table 4. Freundlich isotherm parameters obtained by using the linear regression method.

Linear form	T (K)	283	293	298	303	308
Freundlich-1	$1/n$	0.212	0.214	0.188	0.179	0.152
	K_F	6.92	8.58	10.6	11.0	15.4
	r^2	0.990	0.996	0.991	0.990	0.988
Freundlich-2	$1/n$	0.212	0.214	0.188	0.179	0.152
	K_F	6.92	8.58	10.6	11.0	15.4
	r^2	0.990	0.996	0.991	0.990	0.988

Langmuir parameters obtained from the nonlinear and linear regression methods differed even when compared with the results of Langmuir-1, which had the highest coefficient of determination for any Langmuir isotherm (Tab. 3). Both the Redlich–Peterson and the Freundlich isotherms had almost the same coefficients of determination which were higher than those of Langmuir isotherms (Tab. 5). In addition the Redlich–Peterson and Freundlich isotherms seemed to be the best-fitting models for the experiment results from Fig. 2. Consequently, the Redlich–Peterson and Freundlich isotherms were found to be the suitable isotherm for the adsorption system of phosphorus onto Al_2O_3. Using different linear isotherm forms would significantly affect the coefficient of determination and impact the final determination of parameters, while the application of the nonlinear regression method would avoid such errors.

As shown in Eq. (4), the Redlich–Peterson isotherm has three isotherm constants, namely, A, B, and g ($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized.

Where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \tag{6}$$

i.e., the Langmuir form results. $A = q_m K_a$ and $B = K_a$.
where constants A and B are much greater than unity [5].

$$q_e = \frac{A\,C_e}{B\,C_e^g} = \frac{A}{B}C_e^{1-g} \tag{7}$$

i.e., the Freundlich form results. $A/B = K_F$ and $1 - g = 1/n$.
where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \tag{8}$$

i.e., the Henry's Law form results. $A/(1 + B) = K_H$, K_H is Henry's constant.

Figure 2 shows the plots of experimental data also fitted well with the Freundlich adsorption isotherm of phosphorus onto Al_2O_3 at the temperature of 298 K. Furthermore, compare Eq. (3) with Eq. (7), the values of parameter "K_F" correlated well with "A/B" in a linear relationship as $A/B = 0.988K_F + 0.155$ with 1.000 coefficient of determination, "$1/n$" correlated well with "$1 - g$" ($r^2 = 0.988$) in a linear relationship as $(1 - g) = 0.951\ (1/n) + 0.00836$. At the temperature of 298 K (Fig. 2), the Redlich–Peterson and Freundlich isotherms overlapped with coefficients of determination, $r^2 = 0.992$, which were higher than the case of Langmuir ($r^2 = 0.845$). It indicated that the Redlich–Peterson isotherm was approaching the Freundlich form but not the Langmuir isotherm. Freundlich is a special case of Redlich–Peterson isotherm when constants A and B were much

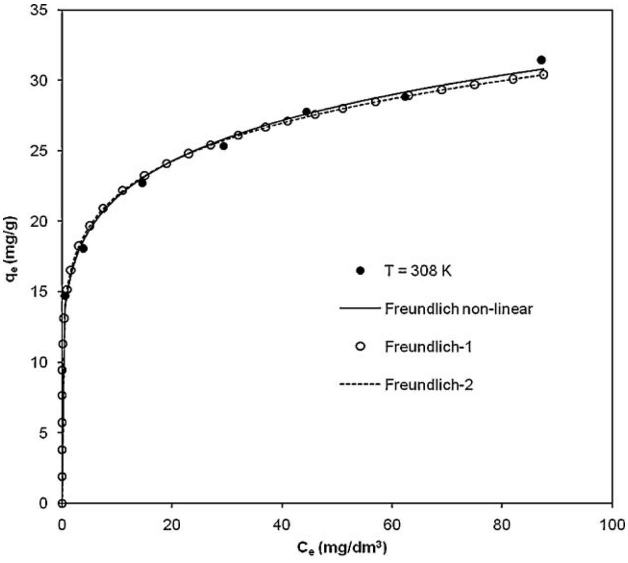

Figure 3. Freundlich isotherms obtained using linear and nonlinear regression methods for the adsorption of phosphorus onto Al_2O_3 at temperature of 308 K.

Table 5. Isotherms parameters obtained by using the nonlinear regression method.

Nonlinear form	T (K)	283	293	298	303	308
Langmuir	q_m (mg/g)	14.8	20.7	21.5	24.3	31.1
	K_a (dm^3/mg)	0.611	0.267	0.464	0.274	0.334
	r^2	0.890	0.888	0.845	0.845	0.817
Freundlich	$1/n$	0.213	0.218	0.200	0.188	0.161
	K_F	6.90	8.49	10.3	10.7	15.0
	r^2	0.985	0.996	0.992	0.988	0.990
Redlich–Peterson	G	0.793	0.782	0.800	0.812	0.839
	B	64.6	2639	63 801	28 198	20 534
	A	455	22 407	654 791	302 759	307 204
	r^2	0.986	0.996	0.992	0.988	0.990

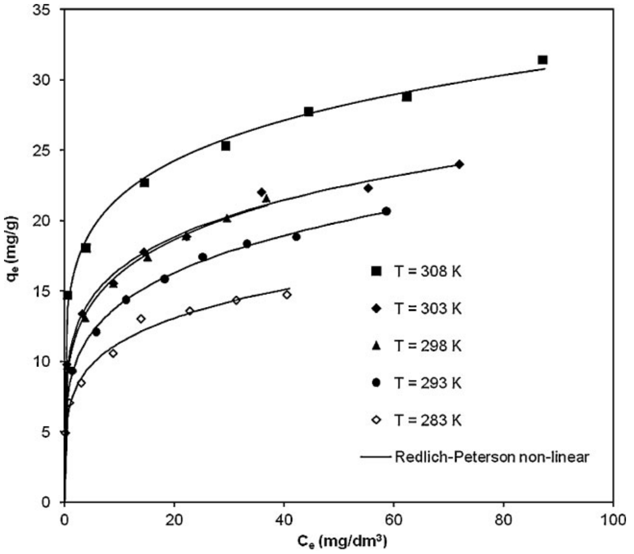

Figure 4. Comparison of Redlich–Peterson isotherms by using the nonlinear regression method for the adsorption of phosphorus onto Al_2O_3 at various temperatures.

bigger than unity [5]. Moreover, the values of g were less than 0.839 and not close to unity. Unlike the linear analysis, different isotherm forms would affect r^2 significantly, and impact the final determination of parameters while nonlinear regression methods would prevent such errors.

3.3 Effect of Temperature on Equilibrium Isotherm

The effect of temperature on the adsorption isotherm is shown in Fig. 4. The results showed that the capacity of the Al_2O_3 for phosphorus adsorption increased with the increase in temperature. It indicated that higher temperatures were suitable for phosphorus uptake from aqueous solution using Al_2O_3.

4 Conclusion

It is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherms for the adsorption of phosphorus onto Al_2O_3. The nonlinear regression method is a better way to obtain the isotherm parameters for this system. Both the Redlich–Peterson and the Freundlich have high coefficients of determination for the adsorption of phosphorus onto Al_2O_3 at various temperatures. A linear relationship was found for Freundlich isotherm parameter "K_F" and Redlich–Peterson isotherm parameters "A/B" as well as "$1/n$" and "$1 - g$" when these two isotherms were overlapped. The capacity of the Al_2O_3 for phosphorus adsorption increased with the increase in temperature, higher temperatures were suitable for phosphorus uptake from aqueous solution using Al_2O_3.

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