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Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents

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ABSTRACT

Adsorption mechanism of a natural compound, alizarin (1,2-dihydroxyanthraquinone), onto three types of microporous polymeric adsorbents (XAD-4, XAD-7, XAD-16) has been proposed using Langmuir, Freundlich and Redlich–Petersen isotherms. Adsorption capacity and optimum adsorption isotherms were predicted by linear least squares and non-linear regression method. Adsorption kinetics was proposed by pseudo-first and second second order models. The adsorption capacity of XAD-16 was the highest at 0.0424 mg/mg, with initial alizarin concentration of 200 mg/L. Pseudo-second-order kinetics was more appropriate in explaining the adsorption mechanism than pseudo-first-order. Over the studied concentration ranges, only XAD-4 adsorption can be reasonably described by the three isotherms. XAD-16 data is only best-fitted to Langmuir and Redlich–Petersen isotherms. Non-linear method proved a better way to predict the equilibrium isotherm parameters. The combination of parameters, such as specific surface area, pore diameter, polarity of the network of the resins, the solubility and polarity of the adsorbate, are the significant parameters for optimum adsorption process.

1. Introduction

Adsorption process involves separation of a substance or adsorbate from one phase, followed by its accumulation onto the surface of the adsorbing phase or adsorbent [1,2]. The sorption ability of different sorbents is strongly dependent on the available surface area, polarity, contact time, pH and the degree of hydrophobic nature of the adsorbent and adsorbate [3,4]. Equilibrium condition is attained when the concentration of the solute remains constant, as a result of zero net transfer of solute adsorbed and desorbed from adsorbent surface. The equilibrium adsorption isotherms describe these relationships between the equilibrium concentration of the adsorbate in the solid and liquid phase at constant temperature [1–3], and also propose the involved interactive forces in the process.

As the isotherm indicates the adsorption capacity of the sorbent, it enables the evaluation of adsorption performance, the involved mechanisms, and parameters to be improved, which are of critical importance in optimizing the use of the adsorbents [2,5]. The prediction of adsorption kinetics is also necessary for the design of sorption systems. While chemical kinetics explains the rate of chemical reaction and the factors affecting the reaction rate, measurement of sorption rate constants could evaluate the basic qualities of a good sorbent such as the time required for a sorbent to remove particular compounds or the efficacy of the sorbents. Pseudo-first- and second-order models are the most common models being used to explain the adsorption kinetics [3,6].

The analysis of experimental equilibrium data by fitting into different isotherm models is an important step to propose suitable model for process design [1]. The most widely applied isotherms for data modeling are the Langmuir and Freundlich, which are developed based on thermodynamic equilibrium [7–9]. Other empirical adsorption models are the Redlich–Petersen [10] and Radke and Prausnitz isotherms [11]. Non-linear method has been suggested a better way to obtain the equilibrium isotherm parameters, but linear regression is most frequently used to investigate the most fitted isotherm [12]. Depending on the way the isotherm equations are linearized, the error distribution changes can either be the best or the worst [13].

In this study, a theoretical model (Langmuir isotherm) and two empirical models (Freundlich and Redlich–Petersen isotherms) were utilized to describe the adsorption of a natural compound, alizarin (1,2-dihydroxyanthraquinones), onto three types of Amberlite polymeric adsorbents—XAD-4, XAD-7 and XAD-16. Anthraquinones (AQs) are natural products that occur in higher plants especially in Rubiaceae family, and also in bacteria, fungi and lichens. AQs and alizarin are used in the production of dyes, and have been reported to exhibit interesting bioactivities, such

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Table 1
Typical properties of Amberlite polymeric adsorbents

Adsorbent	Chemical nature	Polarity	Surface area (m^2/g)	Average pore diameter (Å)
XAD-4	Polystyrene-divinylbenzene	Non-polar	725	40
XAD-7	Methylacrylate ester	Intermediate polarity	450	90
XAD-16	Polystyrene-divinylbenzene	Non-polar	800	100

as antimicrobial, antifungal, hypotensive, analgesic, antimalarial, antioxidant, antileukemic and mutagenic activities [14]. Alizarin is used as a reference compound in the spectrophotometric determination of AQs contents from *Morinda elliptica* cell culture [15]. The adsorption capacity and the optimum equilibrium adsorption isotherm parameters for adsorption of alizarin onto XAD-4, XAD-7 and XAD-16 were estimated by linear least squares and a trial and error non-linear method using Langmuir, Freundlich and Redlich–Petersen isotherms. A comparison was made between these two methods of estimating the isotherm parameters. The adsorption kinetics was proposed based on pseudo-first- and second-order models.

2. Materials and methods

2.1. Adsorbents

Amberlite polymeric adsorbents, XAD-4, XAD-7 and XAD-16 resins (Rohm and Haas Inc., USA), were dried overnight in an oven at 70 °C. The adsorbents were left in a desiccator to reach ambient temperature before sieving to sizes 0.1 cm × 0.1 cm to obtain uniform size distribution. The properties and characteristics of these adsorbents are reported in Table 1.

2.2. Adsorption equilibrium study

The binding capacity of each adsorbent was determined using 0.1 ± 0.02 g adsorbent/30 ml solution of Alizarin in Erlenmeyer flasks. Alizarin was dissolved in dichloromethane to achieve concentration range 20–200 mg/L. The flasks were sealed airtight with aluminium foil and shaken on an orbital shaker (120 rpm) at 24 ± 2 °C. From contact-time experiment, the equilibrium condition was reached within 7–9 h. The pH of the solution throughout the experiment was found consistent at pH 6.5. Adsorbents were incubated in 30 ml alizarin solution at respective concentration. The concentration of alizarin before incubation and at equilibrium was determined spectrophotometrically (Jenway 6300, UK) at 420 nm. The adsorption capacity, q_e (mg/mg), was calculated using

$$q_e = \frac{V_i C_i - V_e C_e}{W} \tag{1}$$

where C_i and C_e are the initial concentration and concentration at equilibrium (mg/L), respectively. V_i and V_e are the initial volume and equilibrium volume (L), respectively, and W is the mass of adsorbent (mg).

The adsorption efficiency was calculated as follows [1]:

$$\text{Adsorption (\%)} = \frac{A_0 - A}{A_0} \times 100 \tag{2}$$

where A_0 and A are the initial and final absorbance (nm) of the solution, respectively.

2.3. Adsorption kinetics

In order to observe the sorption process of alizarin onto the adsorbents, two kinetic models, pseudo-first- and second-order models, were proposed.

2.3.1. Pseudo-first-order Model

The pseudo-first-order equation can be written as

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3}$$

where q_t (mg/g) is the amount of adsorbate absorbed at time t (min), q_e (mg/mg) is the adsorption capacity in equilibrium, and k_f (min^{-1}) is the rate constant for pseudo-first-order model. After integration and by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_f t}{2.303}\right) \tag{4}$$

2.3.2. Pseudo-second-order Model

The pseudo-second-order model can be presented in the following form:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{5}$$

where k_s is the rate constant of pseudo-second-order model (in g/mg min). By definite integration of Eq. (5) for boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$, the following form of equation is obtained:

$$\frac{t}{q_t} = \frac{1}{(k_s q_e^2)} + \left(\frac{1}{q_e}\right) t \tag{6}$$

The initial sorption rate constant, h (mg/g min), at $t = 0$ can be defined as

$$h = k_s q_e^2 \tag{7}$$

2.4. Adsorption isotherm models

The equilibrium adsorption of alizarin onto XAD-4, XAD-7 and XAD-16 resins was analysed using Langmuir, Freundlich and Redlich–Petersen isotherms.

2.4.1. Langmuir isotherm

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites. It is originally developed to represent chemisorption on a set of distinct, localized adsorption sites. Langmuir has developed a theoretical equilibrium isotherm relating the amount of gas adsorbed on a surface due to the pressure of the gas. The equation is applicable to homogeneous adsorption where adsorption process has equal activation energy, based on the following basic assumptions:

(i) molecules are adsorbed at a fixed number of well-defined localized sites,
(ii) each site can hold one adsorbate molecule,
(iii) all sites are energetically equivalent,
(iv) there is no interaction between molecules adsorbed on neighbouring sites.

The general Langmuir equation is as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{8}$$

When linearized, Eq. (8) becomes

$$\frac{C_e}{q_e} = \frac{\alpha_L C_e}{K_L} + \frac{1}{K_L} \tag{9}$$

K_L and α_L are the equilibrium constants of Langmuir equation. Plotting C_e/q_e against C_e yields a straight line with slope, α_L/K_L, and intercept $1/K_L$. The ratio α_L/K_L indicates the theoretical monolayer saturation capacity, Q_0. The shape of the isotherm can determine whether the adsorption is favorable or not.

2.4.2. *Freundlich isotherm*

Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption. The model is given as

$$q_e = K_F C_e^{1/n} \tag{10}$$

If the concentration of solute in the solution at equilibrium, C_e, is raised to the power of *1/n*, with the amount of solute adsorbed being q_e, then $C_e^{1/n}/q_e$ is constant at a given temperature. K_F indicates relative indicator of adsorption capacity, while the dimensionless, $1/n$, is indicative of the energy or intensity of the reaction and suggests the favorability and capacity of the adsorbent/adsorbate system. According to the theory, $n > 1$ represents favorable adsorption conditions. Eq. (10) is linearized into logarithmic form for data fitting and parameter evaluation as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{11}$$

By plotting $\log q_e$ versus $\log C_e$, constant K_F and exponent *1/n* can be calculated.

2.4.3. *Redlich–Petersen isotherm*

Redlich–Petersen developed empirical isotherm with three parameters incorporating the features of the Langmuir and Freundlich isotherms as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{12}$$

where $0 < \beta < 1$.

When $\beta = 1$, the equation gives Langmuir form:

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \tag{13}$$

When $\beta = 0$, the equation follows Henry's Law:

$$q_e = \frac{K_R C_e}{1 + a_R} \tag{14}$$

Eq. (12) may be rearranged into

$$K_R \frac{C_e}{q_e} - 1 = \alpha_R C_e^{\beta} \tag{15}$$

This equation can be linearized by taking logarithms:

$$\ln\left[K_R \frac{C_e}{q_e} - 1\right] = \ln \alpha_R + \beta \ln C_e \tag{16}$$

K_R, α_R and β are the equilibrium constants for Redlich–Petersen equation. It is not possible to obtain the Redlich–Petersen constants by plotting the left-hand side of Eq. (16) against $\ln C_e$, because of the three unknowns—K_R, α_R and β. Therefore, the three parameters can be determined using least-squared fitting procedure to minimize the deviation between theoretically calculated and experimentally measured data [5].

2.5. *Linear and non-linear regression method*

The least squares method for linear regression and non-linear method for non-linear regression were used to fit the experimental data into the models, to obtain the isotherm constants. The non-linear regression method using the solver add-in function of the Microsoft Excel was carried out on the untransformed data. The isotherm parameters were obtained by minimizing the sum of the squared errors (SSE):

$$\mathrm{SSE} = \frac{\sum_{i=1}^{i=N} (q_e^{\mathrm{EXP}} - q_e^{\mathrm{MOD}})^2}{N - D} \tag{17}$$

q_e^{EXP} and q_e^{MOD} are q_e values obtained from experimental data and the model, respectively. N is the number of observation and D is the number of variables in the isotherm. The non-linear regression method requires initial guesses to start the iterations. At least three different initial guesses were performed to have confidence in the solution obtained.

3. Results and discussion

3.1. *Adsorption capacity*

The adsorption of different concentration of alizarin onto microporous polymeric adsorbents is shown in Fig. 1. The maximum adsorption capacities of XAD-4, XAD-7 and XAD-16 for alizarin were 0.0113, 0.0109 and 0.0424 mg alizarin/mg adsorbents, respectively, at the initial alizarin concentration of 200 mg/L. It is evident that XAD-16 resin demonstrated higher adsorptive capacity for alizarin than XAD-7 and XAD-4. XAD-16 has the largest surface area of 800 m^2/g and pore size of 100 Å as compared to XAD-4 and XAD-7 (Table 1). The surface area with respect to pore size generally is the primary determinant of adsorption capacity [16].

Another important factor is the matching of polarity between adsorbent and adsorbate, where adsorbent with higher polarity is more selective for polar compounds. As shown in Fig. 2, XAD-4 and XAD-16 are hydrophobic (with dipole moment of 0.3). There are two potential molecules competing for adsorption sites—the alizarin and dichloromethane. Alizarin, being sparingly soluble in water, dissolved in dichloromethane and should therefore be more readily adsorbed onto non-polar XAD-4 and XAD-16. The possible interaction would be van der Waals' interaction. On the other hand, XAD-7 is relatively more polar (dipole moment = 1.8) which makes the interaction with alizarin minimal if not impossible. The maximum capacity between XAD-4 and XAD-7 was comparable,

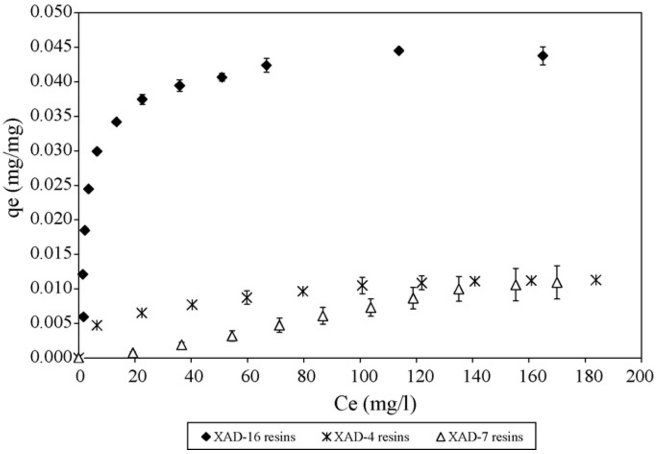

Fig. 1. Equilibrium adsorption isotherms for alizarin on XAD polymeric adsorbents.

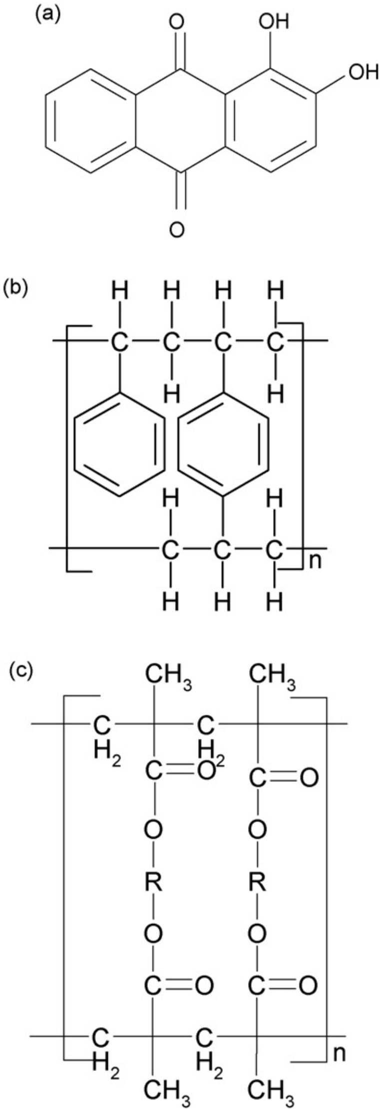

Fig. 2. Chemical structure of (a) alizarin; (b) Amberlite XAD-4/XAD-16 (dipole moment = 0.3); (c) Amberlite XAD-7HP (dipole moment = 1.8).

although the surface area of XAD-4 was almost twice that of XAD-7. This could possibly be due to the smaller pore diameter of XAD-4 which restricts the diffusion of alizarin. Too large a pore diameter on the other hand could render part of the inner adsorbent surface wasted, and the molecules initially adsorbed, prone to desorption at the same time [16]. However, the combination of non-polar chemical structure, large surface area and pore diameter could have made alizarin adsorption and binding more favorable onto XAD-16.

XAD-4 and XAD-16 showed a decrease in efficiency when the concentration of alizarin was increased (data not shown). The efficiency of XAD-4 resins dropped from 70% to 10% when the alizarin concentration was increased from 20 mg/L to 200 mg/L, and the efficiency of XAD-16 dropped from 92% to 67%. Only XAD-7 showed an increased efficiency from 6% to 13%. This shows that the availability of adsorption surface area is an important determining factor to achieve high adsorption efficiency. The adsorption rate of alizarin onto XAD-7 was low due to incompatible hydrophobic molecular interaction with polar adsorbent. As a result, the surface area was not saturated even with increased initial alizarin concentration. Hence, the twofold increase was observed in adsorption efficiency of XAD-7 despite the low adsorption rate. In contrast, alizarin was readily adsorbed onto the surface area of XAD-4 and XAD-16 as alizarin concentration was increased, and the surface became saturated very quickly, resulting in the drop in adsorption efficiency.

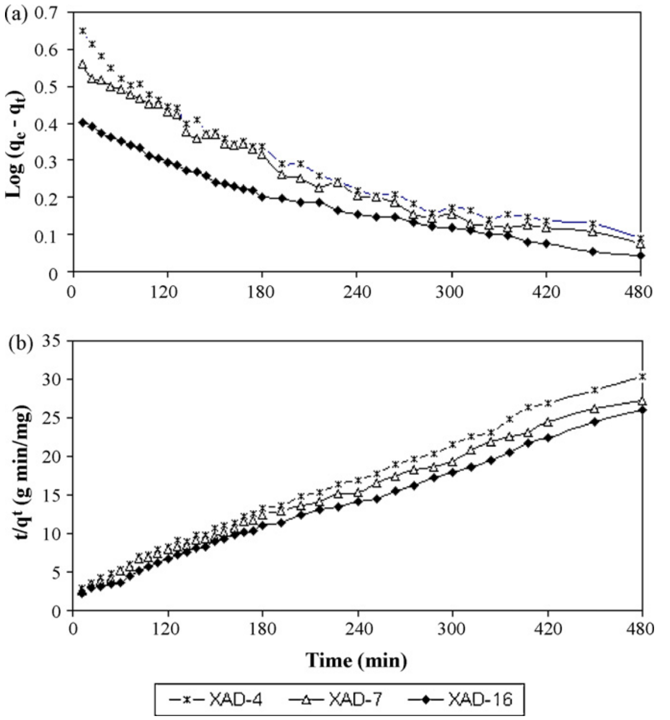

Fig. 3. Kinetics of alizarin sorption onto XAD-4, XAD-7 and XAD-16 based on (a) pseudo-first-order and (b) pseudo-second-order.

3.2. Adsorption kinetics

The adsorption of alizarin from aqueous solution reached a linear phase within an average time period of 480 min, based on contact-time experiment (data not shown). This can be attributed to the utilization of available adsorbing sites on the surface of adsorbent. The sorption of alizarin was almost negligible thereafter possibly due to the slow diffusion of alizarin from the surface film into the micropores, the least accessible sites for adsorption. In order to explain the pseudo-first-order kinetics, adsorption rate constants (k_f) and adsorption capacity (q_e) for the adsorption of alizarin by the polymeric adsorbents were calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ against t (Fig. 3a). The initial sorption rate (h), the equilibrium adsorption capacity (q_e) and the pseudo-second-order rate constants (k_s) were obtained from the slope and intercept of the plots of t/q_t against t (Fig. 3b). Summary of the results are reported in Table 2. Since the calculated correlation coefficients are consistent and closer to unity for pseudo-second-order kinetics model than the pseudo-first-order kinetic model, the adsorption kinetics could be explained well and approximated more favorably by pseudo-second-order kinetic model for the polymeric adsorbents.

3.3. Estimation of isotherm parameters

3.3.1. Linear method

The isotherm equilibrium curves and linear plots are as presented in Figs. 4 and 5, respectively. The comparison of isotherm parameters obtained using linear and non-linear method is shown in Table 3. The regression correlation coefficient R^2 was used to determine the linear equation best fit. As linearized form of the

Table 2
Adsorption kinetics of alizarin by Amberlite polymeric adsorbents

Pseudo-first-order constants	k_f (min^{-1})	q_e (mg/g)	Correlation coefficient (R^2)
XAD-4	0.0019	3.472	0.912
XAD-7	0.0018	3.189	0.939
XAD-16	0.0013	2.276	0.947

Pseudo-second-order constants	h (mg/g min)	k_s (g/mg min)	q_e (mg/g)	Correlation coefficient (R^2)
XAD-4	4.36	52.2	0.289	0.996
XAD-7	4.83	54.7	0.297	0.995
XAD-16	5.08	55.7	0.302	0.998

Redlich–Petersen (RP) isotherm equation contains three unknown parameters—K_R, α_R and β, a minimization procedure was adopted to maximize the coefficient of determination R^2, between the theoretical data for q_e, calculated from the linearized form of RP isotherm equation, and the experimental data [17]. Based on R^2, all the three isotherms describe the best adsorption onto XAD-4. However, for RP isotherm, with R^2 of near unity and the value of $0 < \beta < 1$, XAD-4 and XAD-16 adsorption possibly lie somewhere between the phenomenon as proposed by Langmuir (L) and Freundlich (F) where the adsorption progresses from monolayer to multilayer adsorption on heterogeneous surface. But based on lower values of SSE, RP may describe XAD-7 adsorption better than XAD-16, whereas F isotherm describes the experimental data of XAD-4 better than the others. For F isotherm, $n > 1$ suggests favorable adsorption condition, whereas higher K_F value indicates higher adsorption capacity. XAD-16 showed the highest K_F value and comparable n value for XAD-4 which agrees well with the data obtained (Fig. 1). Although XAD-7 has R^2 value near unity, the n value is actually less than 1. This contradiction may be a result of mathematical complexities and inherent factors related to the distribution of error structure associated with correlation coefficient R^2 in the linear method [13].

3.3.2. Non-linear method

The equilibrium curves and isotherm parameters for XAD-4, XAD-7 and XAD-16 obtained using non-linear method are as shown in Fig. 6 and Table 3, respectively. All the correlation coefficients of the non-linear method are close to unity. The lower SSE values using non-linear method than the linear method imply that the experimental data is represented better by all the three isotherms and that the non-linear method is a better way to calculate the isotherm parameters. Only the isotherm parameters calculated for XAD-4 are comparable to the values obtained by linear method. All isotherms also provide the best fit to XAD-4 and to a lesser extent XAD-7. XAD-16 data is only best-fitted to L and RP isotherm but the data fitness is lesser than XAD-4 and XAD-7. These results based on

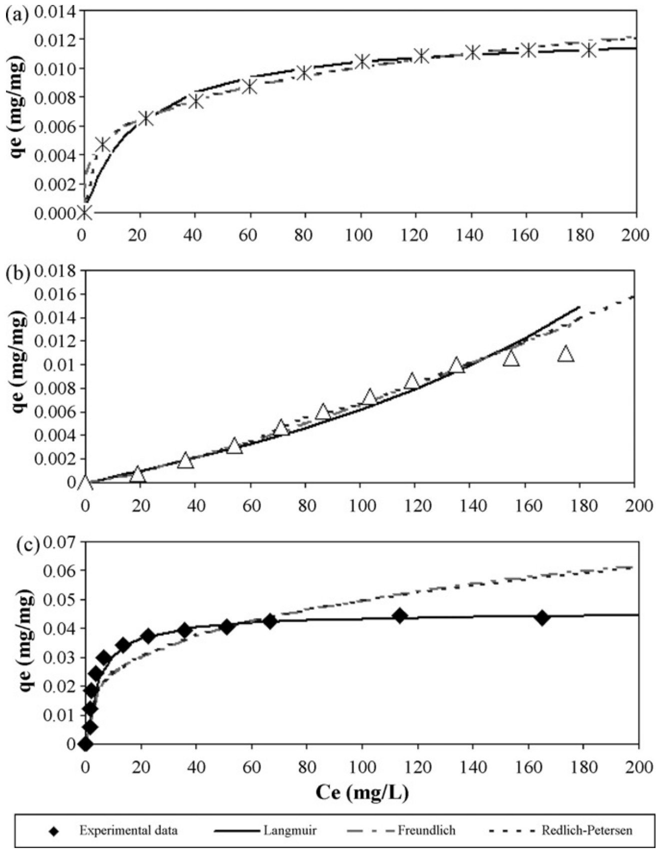

Fig. 4. Equilibrium curves for sorption of alizarin onto (a) XAD-4, (b) XAD-7 and (c) XAD-16 using linear method.

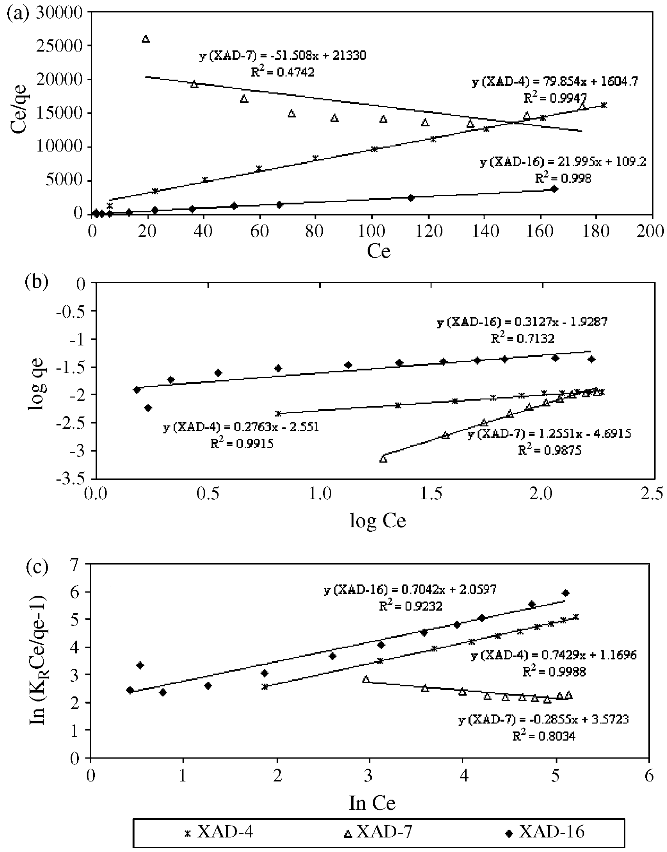

Fig. 5. Linear plots for the sorption of alizarin onto XAD-4, XAD-7 and XAD-16 resins based on (a) Langmuir, (b) Freundlich and (c) Redlich–Petersen isotherm.

Table 3
Isotherm constants for alizarin sorption onto XAD-4, XAD-7 and XAD-16 resins using linear and non-linear method

	Linear			Non-linear		
	XAD-4	XAD-7	XAD-16	XAD-4	XAD-7	XAD-16
Langmuir						
K_L	0.000623	0.000047	0.00916	0.0007	6.85E−05	0.0113
α_L	0.0498	−0.00241	0.201	0.0576	0	0.2524
Q_0	0.0125	−0.0195	0.0455	0.0122	–	0.0448
R^2	0.995	0.474	0.998	0.968	0.992	0.978
SSE	1.35E−06	9.58E−06	2.97E−04	4.45E−07	3.03E−07	8.34E−06
Freundlich						
K_F	2.81E−03	2.03E−05	0.0118	0.0029	5.4E−05	0.0166
n	3.62	0.79	3.2	3.72	1	4.63
R^2	0.992	0.988	0.713	0.992	0.991	0.907
SSE	9.34E−07	4.97E−06	5.56E−04	9.04E−08	2.89E−07	3.41E−05
Redlich–Petersen						
K_R	0.01	0.0007	0.1	0.0092	6.88E − 05	0.0113
α_R	3.22	35.5984	7.84	2.91	0.0051	0.252
β	0.743	−0.2855	0.704	0.747	0.005	1.00
R^2	0.999	0.8034	0.923	0.993	0.992	0.978
SSE	1.10E−06	6.09E−06	5.95E−04	9.46E−08	3.46E−07	9.27E−06

linear and non-linear method suggest that only XAD-4 adsorption can be reasonably described by the three isotherms.

The isotherm constants of a non-linear equation obtained from its linear form may introduce large errors and did not correlate the original isotherm equation well with experimental equilibrium data points. Using SSE in non-linear method, a uniform error distribution (irrespective of the linear form) for the whole range of experimental data is obtained and this is better for data fitness. The problem with the transformation of non-linear to linear expression is the distortion of experimental error. This gives rise to the difference in predicted and experimental equilibrium data by linear and non-linear methods. The linear method assumes the scatter of points around the line, follows a Gaussian distribution, and the error distribution is the same at every value of X [13]. This is rarely true or practically impossible with equilibrium isotherm models (as most of the isotherm models are non-linear). The error distribution gets altered after transforming the data into a linear form and different isotherm would affect R^2 significantly due to different axial settings. This would impact the final determination of isotherm parameters.

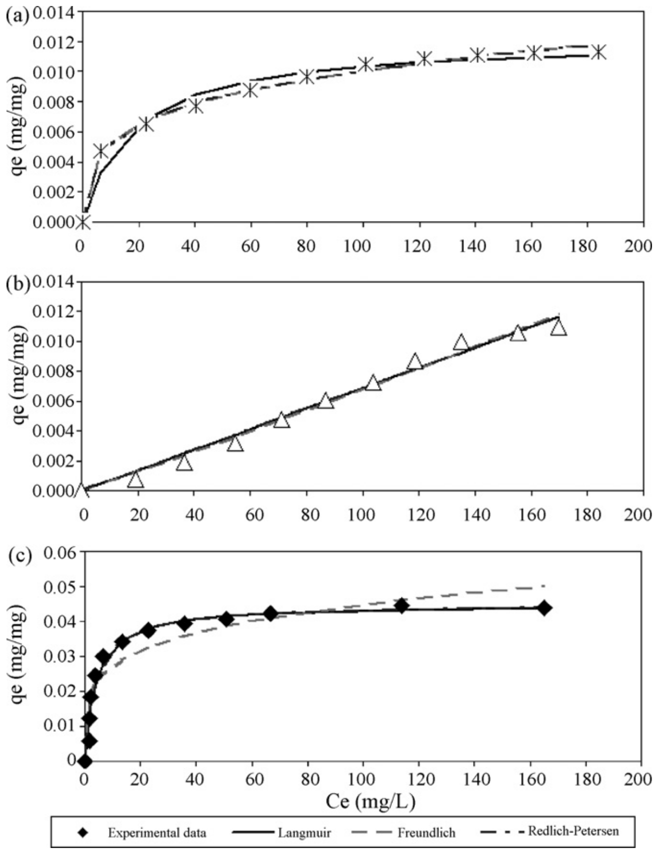

Fig. 6. Equilibrium curves for sorption of alizarin onto (a) XAD-4, (b) XAD-7 and (c) XAD-16 resins using non-linear method.

With non-linear method, such errors could be avoided. Although the approach in which the unknown parameters in the function are estimated is theoretically the same, non-linear least squares regression has much larger, more general class of functions and can generate good estimates of the unknown parameters in the model with relatively small data sets. Almost any function that can be written in a closed form can be incorporated into a non-linear regression model. Unlike linear regression, there are very few limitations on the way parameters can be used in the functional part of a non-linear regression model. This study proves that non-linear method is a more appropriate technique to obtain the isotherm parameters.

4. Conclusion

The study on the equilibrium adsorption isotherm provides greater insights on the separation process, and in optimizing the separation efficiency. XAD-16 demonstrated the highest adsorption capacity with 0.0424 mg/mg at the initial alizarin concentration of 200 mg/L. Pseudo-second-order model is more appropriate in order to explain the adsorption kinetics. High specific surface area, appropriate pore diameter and polarity of the network of the resins, including the solubility and polarity of adsorbate, play synergistic role during the adsorption process. Based on linear and non-linear method, only XAD-4 adsorption can be reasonably described by the three isotherms. XAD-16 data is only best-fitted to Langmuir and Redlich–Petersen isotherms. Although linear regression was frequently used to determine the most fitted isotherm, non-linear method proved a better way to predict the equilibrium isotherm parameters in this study as lower SSE values were obtained. The present study could pave the way towards greater understanding of the important adsorption parameters for the recovery of total anthraquinones from cell culture system.

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