

The Elovich isotherm equation: Back to the roots and new developments

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Abstract

This work seeks to debunk the claim that the Elovich isotherm is vastly inferior to the Langmuir or Freundlich isotherm in the correlation of adsorption equilibrium data. This mistaken finding, reported in many published articles, is a result of comparing linearized versions of the three isotherms, which are based on different sets of transformed data. When isotherm discrimination is performed on the basis of untransformed data (the conventional adsorbed phase concentration versus solution phase concentration plot), the Elovich isotherm is shown to be highly and consistently competitive against the Langmuir or Freundlich isotherm. Predictions of untransformed data can be obtained from the three isotherms by using parameter estimates generated by either linear or nonlinear regression. To promote a wider application of the

Elovich isotherm in adsorption research, this work shows how a modified form of the Elovich isotherm can be used to evaluate the energy distribution of heterogeneous surfaces.

Keywords: Energy distribution; Equilibrium data; Implicit isotherm; Isotherm comparison; Isotherm ranking; Lambert W function.

1. Introduction

A variety of isotherm models are used to correlate liquid phase adsorption equilibrium data. Some of these isotherm models may offer mechanistic interpretations, but the majority of studies seek to identify the best fitting model. Although statistical experimental designs have been recommended for isotherm discrimination [1], most studies employ simple goodness-of-fit measures such as the coefficient of determination R^2 to rank isotherm equations. The equations of Freundlich and Langmuir have historically been compared and are still being compared by many investigators. Irving Langmuir was the first scientist to tackle the problem of choosing between his namesake equation and the Freundlich equation. In a 1918 paper, Langmuir applied his newly proposed equation and the Freundlich equation to several gas adsorption data sets [2]. He plotted the data in the form of p/q versus p , where p is the equilibrium gas pressure and q is the amount of gas adsorbed. A logarithmic transformation was used to linearize the Freundlich equation. Straight lines were drawn manually to pass as nearly as possible through the transformed data. Although R^2 values were not calculated for the linear fits, Langmuir concluded that the linearized form of his equation outperformed the linearized version of the Freundlich equation.

Today, researchers are not restricted to choosing between the Freundlich and Langmuir equations as the pool of isotherm models has expanded considerably. Some commonly used ones include the equations of Dubinin and Radushkevich, Temkin, and Elovich. One reason for the appeal of these two-parameter isotherms is that, like the Freundlich and Langmuir

equations, they can be transformed into linear forms, and linear regression can then be used for data correlation and parameter estimation. Table 1 presents some recent studies in which linearized versions of the Freundlich, Langmuir, Dubinin–Radushkevich, Temkin, and Elovich equations (plus a few others) have been evaluated and ranked on the basis of R^2 scores [3–28]. As can be seen in Table 1, in the majority of cases, the linearized Langmuir equation was the best performing model, while the linearized Freundlich equation was also quite effective. It is significant that in the cases listed in Table 1, in no instance has the linearized Elovich equation been ranked first. In fact, of the 56 cases of isotherm comparison, the Elovich equation has been ranked last in 31 cases (55%). The isotherm ranking results in Table 1 unequivocally show that the linearized Elovich equation is much inferior to the linearized Freundlich or Langmuir equation.

The motivation of the present study is to rehabilitate the sullied image of the Elovich equation in the modeling of water contaminant adsorption by solid materials. We seek to demonstrate that, despite the convincing body of evidence presented in Table 1, the Elovich equation is not in any way inferior to the Freundlich or Langmuir equation. By making use of literature adsorption data for four water contaminants (sulfadiazine, methylene blue, chromium, and reactive blue-4), we show that a flawed method has been used in previous studies to compare the three isotherms. Specifically, the practice of ranking the three isotherms according to the R^2 scores for linear fits leads to erroneous conclusions. When the three isotherms are compared on the basis of untransformed data (adsorbed phase concentration versus solution phase concentration), the resulting R^2 values reveal that the Elovich equation is highly and consistently competitive against the Freundlich or Langmuir equation.

Furthermore, although many researchers have applied the Elovich equation in their work, very few are aware of its theoretical derivation, which was published in a little-cited French paper. As such, the secondary aim of this work is to provide some background

information on the theoretical foundation of the Elovich equation and to promote the citation of its original source. Finally, we describe a new application of the Elovich equation in adsorption research. For the first time, we show how a hybrid model, called the “Langmuir–Elovich isotherm”, can be used to evaluate the energy distribution of adsorption sites existing on energetically heterogeneous surfaces.

Table 1. Discrimination of linearized adsorption isotherms reported in some recent studies. ^a

Ref.	No. of data sets	Isotherm ranking based on R^2 scores						
		1st	2nd	3rd	4th	5th	6th	7th
Joshi and Kumar [3]	3	L	F	E				
		F	L	E				
		L	F	E				
Abbas [4]	1	T	L	E	F			
Zulfiqar et al. [5]	1	L	F	T	E			
Biswal et al. [6]	1	T	L	DR	E	F		
Tewari et al. [7]	1	To	L	T	F	E		
Taghavi et al. [8]	1	LF	F	L	T	RP	E	
Jana et al. [9]	1	F	L	E				
Ozcelik et al. [10]	1	F	L	T	E			
Meng et al. [11]	6	F	T	L	E	DR		
		L	T	F	DR	E		
		F	T	L	DR	E		
		L	T	F	E	DR		
		T	L	F	DR	E		
		T	L	F	DR	E		
Yu et al. [12]	3	L	E	F				
		L	F	E				
		F	L	E				
Nikzad et al. [13]	1	LF	F	T	L	E		
Zulfiqar et al. [14]	1	L	F	E	T	DR		
Manjunath et al. [15]	3	L	F	DR	T	E		
		L	F	T	DR	E		
		L	F	E	T	DR		
Xie et al. [16]	1	L	DR	T	E	H	F	HJ
Moosavi et al. [17]	2	L	F	E				
		L	F	E				
Abbas [18]	2	L	RP	F	T	E		
		L	F	T	E			
Ordonez et al. [19]	6	L	T	F	ML	J	E	
		J	L	F	ML	T	E	
		T	L	F	J	ML	E	
		T	L	J	F	E	ML	
		ML	L	F	T	E	J	

		T	F	L	J	E	ML
Saxena et al. [20]	1	L	T	RP	F	E	
Patil et al. [21]	1	L	F	T	E		
Zulfiqar et al. [22]	1	L	F	E	T	DR	
Singh et al. [23]	4	DR	RP	E			
		DR	E	RP			
		DR	E	RP			
		DR	E	RP			
Gupt et al. [24]	3	L	E	F			
		L	E	F			
		L	E	F			
Jabłońska [25]	6	LF	L	DR	E	F	T
		LF	DR	L	F	E	T
		LF	DR	L	F	E	T
		LF	L	DR	E	F	T
		LF	L/DR	–	F	E	T
		LF	L	T	DR	F	E
Joshi et al. [26]	3	F	L/T	–	E		
		F	E	T	L		
		F	T	L	E		
Sahoo et al. [27]	1	L	F	T/E			
Panda et al. [28]	1	F	T	L	E		

^a DR: Dubinin–Radushkevich; E: Elovich; F: Freundlich; H: Halsey; HJ: Harkins–Jura; J: Jovanovic; L: Langmuir; LF: Langmuir–Freundlich; ML: Modified Langmuir; RP: Redlich–Peterson; T: Temkin; To: Toth.

2. Isotherm equations

2.1. The original Elovich isotherm

A literature search reveals that a 1991 paper published by Dusart et al. [29] is the original source of the Elovich isotherm. As an aside, we mention that it was not difficult to accurately pinpoint the original source because one of us (JCB) has personal knowledge of the research work by Dusart et al. conducted at the University of Limoges in the early 1990s. To derive the Elovich isotherm, Dusart et al. [29] adopted the kinetic argument of Langmuir [2] for the simple reaction defined by Eq. (1), where A is a chemical substance and S is a solid surface capable of adsorbing A .



In Langmuir's kinetic theory for saturable adsorption of gases to solid surfaces, adapted for aqueous adsorption systems (the original partial pressure term is replaced by the solution phase concentration term), the rate of adsorption on the surface (r_a) is given by Eq. (2), and the rate of desorption from the surface (r_d) is given by Eq. (3), where k_a is the rate coefficient in the forward direction, c is the solution phase concentration, θ is the fraction of the surface covered, and k_d is the reverse rate coefficient. Equating the rate of adsorption and the rate of desorption gives us the celebrated Langmuir isotherm.

$$r_a = k_a c (1 - \theta) \quad (2)$$

$$r_d = k_d \theta \quad (3)$$

Dusart et al. [29] made one major change to Langmuir's kinetic argument: they replaced the original rate of adsorption defined by Eq. (2) with Eq. (4), which dictates that the rate of adsorption decreases exponentially with increasing θ . At equilibrium, the rate of adsorption must equal the rate of desorption, so we obtain Eq. (5).

$$r_a = k_a^* c \exp(-\theta) \quad (4)$$

$$k_a^* c \exp(-\theta) = k_d \theta \quad (5)$$

Rearranging Eq. (5) yields Eq. (6). If we define $k_a^*/k_d = b_E$ and $\theta = q/q_E$, where b_E is an equilibrium constant, q is the adsorbed phase concentration, and q_E is the adsorption capacity, Eq. (6) may be rewritten as Eq. (7). Dusart et al. [29] called Eq. (7) the Elovich isotherm because the exponential function used in Eq. (4) was often attributed to Elovich in the catalysis literature. However, the exponential function was first proposed by Roginsky and Zeldovich [30,31]. Consequently, the "Elovich isotherm" label adopted for Eq. (7) is a misnomer.

$$\theta = \frac{k_a^*}{k_d} c \exp(-\theta) \quad (6)$$

$$q = q_E b_E c \exp\left(-\frac{q}{q_E}\right) \quad (7)$$

Dusart et al. [29] rearranged Eq. (7) to the form given by Eq. (8), which is linear in the two parameters. If $\ln(q/c)$ is plotted as a function of q , the slope is equal to $-1/q_E$ and the intercept gives $\ln(q_E b_E)$.

$$\ln\left(\frac{q}{c}\right) = \ln(q_E b_E) - \frac{1}{q_E} q \quad (8)$$

Dusart et al. [29] used the linearized Elovich equation to describe the adsorption of amino acids by activated carbon. A follow-up study published in 1995 by Ferrandon et al. [32] applied the linearized expression to the adsorption data of several water pollutants. (For information: the first author of both references [29] and [32] is one and the same person. Indeed, after her divorce, the married Odile Dusart took back her maiden's name to become Odile Ferrandon.) It seems that the two papers [29,32] attracted little or no attention, and the Elovich equation lay dormant until the mid-2000s when Meçabih et al. [33], Hamdaoui [34], and Hamdaoui and Naffrechoux [35] used the linearized Elovich expression to fit the adsorption data of several water contaminants. Subsequently, Ncibi [36] and Ncibi et al. [37] used both the linear and nonlinear versions of the Elovich equation to describe the adsorption data of dyes. Today, when using the Elovich equation to fit water contaminant adsorption data, the linearized form is preferred.

2.2. The Langmuir–Elovich isotherm, a new model

The original Elovich equation, Eq. (7), is implicit in q . It can be inverted by means of the Lambert W function [38,39] to yield an expression explicit in q , as shown in Eq. (9), where W denotes the Lambert W function with argument $b_E c$. When $q = q_E$, $W(b_E c) = 1$, so that $c = \exp(1)/b_E$. So, q_E is less than Langmuir's saturation capacity parameter q_m [Eq. (11)].

$$q = q_E W(b_E c) \quad (9)$$

It has been shown that most adsorption isotherms arise from statistical distributions of binding energies [40]. However, the original Elovich equation does not allow one to compute

such a distribution since q tends to infinity, just like with the Freundlich equation. To overcome this problem, we define a “Langmuir–Elovich” equation in the form of the Langmuir–Freundlich equation and the loading-explicit Elovich equation. The final expression is given by Eq. (10), where b_E is the binding constant and $L = q_E/q_m$ is such that $0 < L < 1$. This equation reduces to the original form at the lowest concentrations and/or lowest values of L .

$$q = \frac{q_m L \cdot W(b_E c)}{1 + L \cdot W(b_E c)} \quad (10)$$

2.3. The Langmuir and Freundlich isotherms

For the data fitting examples examined in this work, the Elovich equation is compared to the Langmuir [Eq. (11)] or Freundlich equation [Eq. (12)]. In these two equations, q_m , b_L , K , and n are adjustable parameters. These parameters are usually treated as empirical, but they can also be interpreted in a physical sense, e.g., as free energies of adsorption.

$$q = \frac{q_m b_L c}{1 + b_L c} \quad (11)$$

$$q = K_F c^{n_F} \quad (12)$$

In the environmental adsorption literature, the Langmuir and Freundlich isotherms are frequently linearized so that linear regression can be used to fit adsorption data. Eqs. (13) and (14) are two commonly used linear versions of the Langmuir equation, while Eq. (15) is the well-known logarithmic transformation of the Freundlich equation. Note that Eq. (14) was originally proposed by Langmuir [2].

$$\frac{1}{q} = \frac{1}{q_m b_L c} + \frac{1}{q_m} \quad (13)$$

$$\frac{c}{q} = \frac{1}{q_m} c + \frac{1}{q_m b_L} \quad (14)$$

$$\ln(q) = n_F \ln(c) + \ln(K_F) \quad (15)$$

2.4. Isotherm fitting and evaluation

The isotherm equations considered in this work (Elovich, Langmuir, and Freundlich) were fitted to previously published experimental data using linear or nonlinear regression. In the regression procedure, the sum of squared residuals (SSR) is minimized. The SSR, given here by Eq. (16), is defined as the difference between the measured and calculated adsorbed phase concentrations. In Eq. (16), $q_{i,obs}$ is the i th observed adsorbed phase concentration, $q_{i,fit}$ is the i th adsorbed phase concentration calculated from a particular isotherm, and m is the number of data points.

$$SSR = \sum_{i=1}^m (q_{i,obs} - q_{i,fit})^2 \quad (16)$$

Since the Elovich, Langmuir, and Freundlich equations contain the same number of adjustable parameters, it is not necessary to use information-theoretic metrics such as the Akaike Information Criterion for isotherm comparison. As such, the coefficient of determination (R^2) and the root mean square error (RMSE) are used as statistical indicators of the quality of fit.

3. Results and discussion

This section has two parts. The first part seeks to debunk the mistaken conclusion that the Elovich equation is inferior to the Langmuir or Freundlich equation. To do this, four cases taken from Table 1 are examined to verify the reported inferiority of the linearized Elovich equation. An exposition is then presented, outlining why the inferiority of the Elovich equation is due to the use of a flawed method to compare the isotherms. Finally, the practicality of comparing nonlinear versions of the three isotherms is explored. The second part introduces a modified form of the Elovich equation, termed the “Langmuir–Elovich isotherm”, which is used to evaluate the energy distribution of heterogeneous adsorbents.

3.1. Cases 1 and 2: Langmuir versus Elovich

Case 1 is based on an experimental and modeling study on the adsorption of three antibiotics (sulfadiazine, metronidazole, and tetracycline) by an activated carbon adsorbent [15]. The authors used five isotherms (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Elovich) to correlate the measured equilibrium data. In the data fitting process, linear forms of the five isotherms were used. For all three antibiotics, the linearized Langmuir equation given by Eq. (13) was found to be the most effective isotherm, outperforming the linearized Elovich equation given by Eq. (8). Fig. 1 shows the linear fits of the Langmuir and Elovich equations to one of the three antibiotics (sulfadiazine). As can be seen in Fig. 1A, the Langmuir fit is satisfactory, returning an R^2 score of 0.993. In contrast, Fig. 1B shows that the Elovich fit is rather poor, returning an R^2 value of 0.898. The best-fitting sets of parameters obtained by the two fits are presented in Table 2. Fig. 1 confirms the finding of the original study [15], i.e., the Langmuir fit is superior to the Elovich fit.

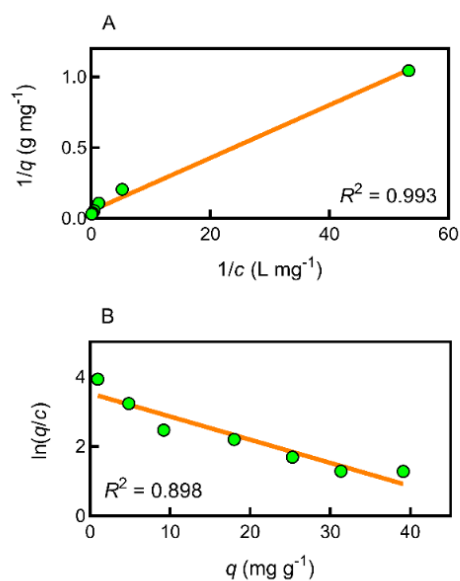


Fig. 1. Linear fits of sulfadiazine adsorption data [15]. (A) Langmuir, Eq. (13). (B) Elovich, Eq. (8).

Table 2. Fitted parameters and statistical metrics for the linear fits plotted in Figs. 1–4. ^a

Case	Linearized isotherm	Parameter	Statistical metric
1	Langmuir, Eq. (13)	$q_m = 18.57; b_L = 2.88$	$R^2 = 0.993; \text{RMSE} = 0.03$
	Elovich, Eq. (8)	$q_E = 15.03; b_E = 2.26$	$R^2 = 0.898; \text{RMSE} = 0.30$
2	Langmuir, Eq. (14)	$q_m = 439.7; b_L = 0.39$	$R^2 = 0.991; \text{RMSE} = 0.007$
	Elovich, Eq. (8)	$q_E = 87.59; b_E = 8.85$	$R^2 = 0.818; \text{RMSE} = 0.82$
3	Freundlich, Eq. (15)	$n_F = 0.23; K_F = 11.67$	$R^2 = 0.986; \text{RMSE} = 0.05$
	Elovich, Eq. (8)	$q_E = 5.05; b_E = 26.31$	$R^2 = 0.931; \text{RMSE} = 0.37$
4	Freundlich, Eq. (15)	$n_F = 0.38; K_F = 37.25$	$R^2 = 0.989; \text{RMSE} = 0.05$
	Elovich, Eq. (8)	$q_E = 31.22; b_E = 4.51$	$R^2 = 0.894; \text{RMSE} = 0.27$

^a q_m, q_E (mg g^{-1}); b_L, b_E (L mg^{-1}); n_F (-); K_F ($\text{L}^{n_F} \text{mg}^{(1-n_F)} \text{g}^{-1}$); RMSE (mg g^{-1}).

In case 2, linearized versions of the Langmuir, Freundlich, Temkin, Redlich–Peterson, and Elovich equations were used to describe the adsorption of the dye methylene blue by a carbon nanotube material [20]. The data fitting results of the original study showed that the Langmuir equation outperformed the other four isotherms, with the Elovich equation being the worst performer. Here, the methylene blue data were fitted to the linearized Langmuir equation given by (14) and the linearized Elovich equation given by Eq. (8). With an R^2 value of 0.991, the Langmuir fit shown in Fig. 2A tracks the experimental data well. Fig. 2B shows that the Elovich fit is markedly inferior to the Langmuir fit, returning an R^2 value of 0.818. Fig. 2 verifies the finding of the original study [20], i.e., the Elovich fit is inferior to the Langmuir fit. The parameter estimates obtained by the two fits are listed in Table 2.

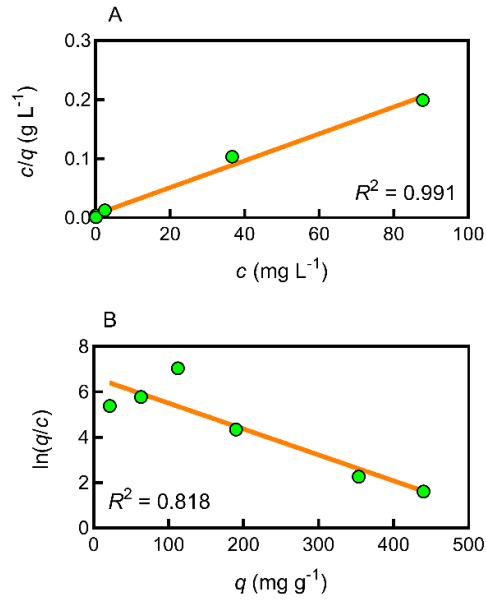


Fig. 2. Linear fits of methylene blue adsorption data [20]. (A) Langmuir, Eq. (14). (B) Elovich, Eq. (8).

3.2. Cases 3 and 4: Freundlich versus Elovich

Case 3 describes the adsorption of hexavalent chromium by a modified textile fabric material [10]. The authors fitted the Langmuir, Freundlich, Temkin, and Elovich equations to the chromium adsorption data, reporting that the linearized Freundlich [Eq. (15)] and Elovich [Eq. (8)] equations were the best and worst isotherms, respectively. Fig. 3 shows the fits of the Freundlich ($R^2 = 0.986$) and Elovich ($R^2 = 0.931$) equations to the chromium data, confirming that the former is indeed superior to the latter.

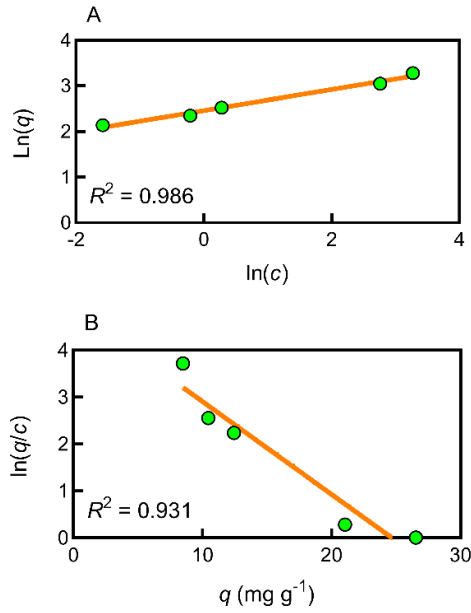


Fig. 3. Linear fits of chromium adsorption data [10]. (A) Freundlich, Eq. (15). (B) Elovich, Eq. (8).

Case 4 is based on a study on the adsorption of the anionic dye reactive blue-4 by a metal organic framework material [28]. Four isotherms (Langmuir, Freundlich, Temkin, and Elovich) were fitted to the dye adsorption data. According to the original study [28], the linearized Freundlich equation given by Eq. (15) outperformed the other three isotherms, and the linearized Elovich equation given by Eq. (8) was the least effective. Fig. 4 shows the fits of the linearized Freundlich and Elovich equations to the dye data. Fig. 4 corroborates the claim of the original study [28], i.e., the Elovich fit ($R^2 = 0.894$) is inferior to the Freundlich fit ($R^2 = 0.989$). The best-fitting sets of parameters for cases 3 and 4 are given in Table 2.

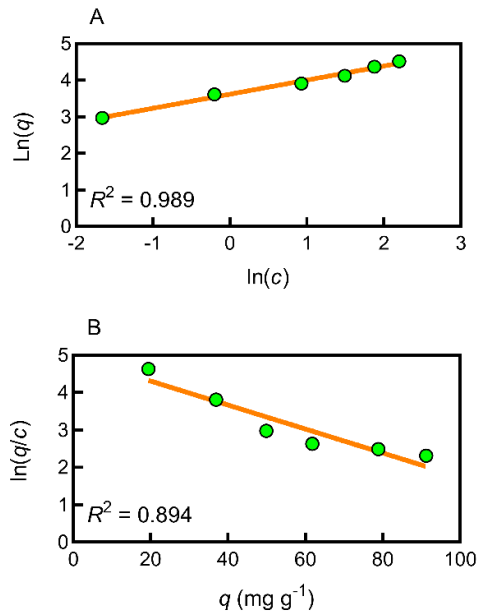


Fig. 4. Linear fits of reactive blue-4 adsorption data [28]. (A) Freundlich, Eq. (15). (B) Elovich, Eq. (8).

3.3. Unbiased comparison of isotherms

In cases 1–4, it can be seen that the linearized Elovich equation is clearly inferior to the linearized Langmuir and Freundlich equations in correlating the experimental isotherms of sulfadiazine, methylene blue, hexavalent chromium, and reactive blue-4. In all cases, the R^2 values for the Langmuir and Freundlich fits are > 0.98 , while those for the Elovich fits range from a low of 0.82 to a high of only 0.93.

However, it is argued that the inferiority of the Elovich equation is due to the use of a flawed method to compare the isotherms. It is inappropriate to compare the R^2 values for the linear fits because the linear regression procedure was applied to different sets of transformed data. For example, in case 1, the R^2 value of 0.993 indicates the ability of the linearized Langmuir equation [Eq. (13)] to fit the data trend exhibited by the transformed variables $1/q$ and $1/c$. The R^2 score of 0.898 tells us the ability of the linearized Elovich equation [Eq. (8)] to

fit the data profile depicted by the transformed variable $\ln(q/c)$ and the untransformed variable q .

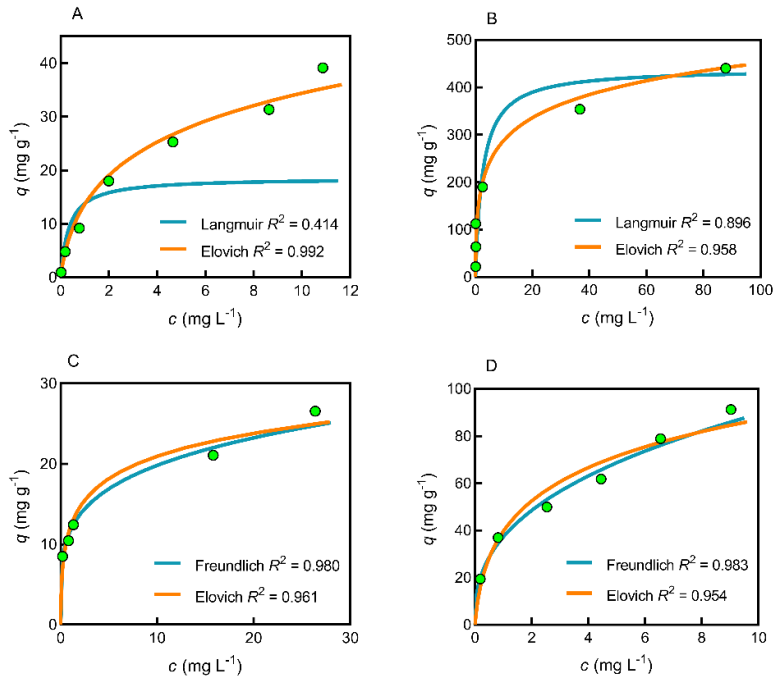


Fig. 5. Comparison of adsorption data and q versus c curves calculated using parameter estimates obtained by the linear fits plotted in Figs. 1–4. (A) Case 1. (B) Case 2. (C) Case 3. (D) Case 4.

To obtain unbiased results, different isotherms should be compared *on the basis of common variables*. One method of doing this is to evaluate how well different isotherms describe the data trends exhibited by the untransformed variables q and c . For case 1, Fig. 5A shows the q versus c curve calculated from the untransformed Langmuir equation [Eq. (11)] using the parameter estimates obtained by the linearized Langmuir fit (Table 2, case 1). Also shown in Fig. 5A is the q versus c curve calculated from the untransformed Elovich equation [Eq. (7)] using the parameter estimates produced by the linearized Elovich fit (Table 2, case 1). The q versus c curves for the isotherms evaluated in the other three cases can be calculated in

the same manner, using the parameter estimates obtained by the respective linear fits given in Table 2, and they are presented in Figs. 5B–5D. New R^2 values calculated for all q versus c curves are shown in Fig. 5.

For case 1, Fig. 5A shows that the q versus c curve calculated using the parameter estimates produced by the linearized Langmuir fit deviates significantly from the data trend ($R^2 = 0.424$). In particular, data points at high concentrations are poorly described. In contrast, the q versus c curve calculated using the parameter estimates obtained by the linearized Elovich fit closely tracks the data trend ($R^2 = 0.992$). The result of Fig. 5A is the complete opposite of the result of Fig. 1. Going from Fig. 1 to Fig. 5A, we see a huge drop in the performance of the Langmuir equation but a significant enhancement in the performance of the Elovich equation.

Similar observations can be made for case 2. Fig. 5B shows that the q versus c curve calculated using the parameter estimates produced by the linearized Langmuir fit cannot capture the overall shape of the data trend ($R^2 = 0.896$). The q versus c curve calculated using the parameter estimates obtained by the linearized Elovich fit matches the data trend quite well ($R^2 = 0.958$). Therefore, the result of Fig. 5B contradicts the result of Fig. 2. In summary, Figs. 5A and 5B show that the Elovich equation is superior to the Langmuir equation in tracking the untransformed data of sulfadiazine and methylene blue, which are expressed in the form of q versus c .

For case 3, Fig. 5C shows that the q versus c curve calculated using the parameter estimates obtained by the linearized Freundlich fit traces the data trend well ($R^2 = 0.980$). Likewise, the q versus c curve calculated using the parameter estimates produced by the linearized Elovich fit agrees quite well with the data trend ($R^2 = 0.961$). The result for case 4, as shown in Fig. 5D, is essentially the same as that for case 3. Although Figs. 3 and 4 suggest that the linearized Freundlich equation is much superior to the linearized Elovich equation in describing the transformed data of chromium and reactive blue-4, Figs. 5C and 5D indicate that

there are only slight differences between the two equations in tracing the same adsorption data expressed in the form of q versus c .

When plotting the linearized Langmuir data as $1/q$ versus $1/c$ (Fig. 1) or c/q versus c (Fig. 2), a part of the experimental data points is grouped together, and this will contribute to giving a bias to the regression, although its R^2 value is artificially excellent. Note that the representation of the Langmuir equation in Fig. 1 was considered the worst fitting approach [41], and this can cause important deviations when trying to trace the direct Langmuir isotherm q versus c again (as in Fig. 5A). As for the linearization of the Freundlich equation, it involves the logarithms of the two experimental values, as can be seen in Figs. 3 and 4. There is little deviation in the recalculated curves (Figs. 5C and 5D), probably because a suitable range of data is used [41].

Taken together, Fig. 5 clearly shows that the Elovich equation is not markedly inferior to the Langmuir or Freundlich equation, contradicting the results of Figs. 1–4. Although the linearized Elovich equation is rather poor at fitting the transformed data, the resulting parameter estimates are surprisingly useful. They allow the Elovich equation to accurately track the untransformed data of q versus c , easily outperforming the Langmuir equation and closely matching the performance of the Freundlich equation. Of the papers reviewed (Table 1) for this study, none have investigated the ability of the three isotherms to describe data trends plotted in the form of q versus c .

3.4. Comparison of nonlinear isotherms

As discussed in Section 3.3, an impartial way to compare the Elovich, Langmuir, and Freundlich equations is by assessing their ability to describe isotherm data expressed in the direct form of q versus c . There is little or no merit in comparing the ability of their linearized versions to describe various types of transformed data. Therefore, it makes sense to fit their original functional forms to the adsorption data depicted in Fig. 5, which are expressed in the

form of q versus c . Given that the three isotherms are nonlinear in their parameters, this data fitting approach requires the use of an iterative algorithm to minimize the SSR defined by Eq. (16).

In the case of the Langmuir or Freundlich equation, the value of $q_{i,fit}$ in the SSR can be easily calculated from Eq. (11) or (12). However, obtaining $q_{i,fit}$ from the Elovich equation is somewhat cumbersome because q in Eq. (7) appears on both sides of the equation. In other words, the Elovich equation is implicit in q . Therefore, it is necessary to incorporate a numerical scheme within the least-squares fitting algorithm to calculate $q_{i,fit}$ at each iteration. Software packages such as MATLAB and Mathematica provide a convenient way to implement such a least-squares fitting procedure. In this work, the loading-implicit Elovich equation was fitted to isotherm data using Mathematica. The nonlinear least-squares fitting was provided by the command `NonlinearModelFit`, while $q_{i,fit}$ was estimated at each iteration using the command `FindRoot`, which uses Newton's method to solve Eq. (7).

Although the Elovich equation is treated as an expression implicit in q in the least-squares fitting method described above, it is actually possible to convert the loading-implicit expression to a form that is explicit in q . The inversion of the loading-implicit Elovich equation is achieved by means of the Lambert W function, as explained in Section 2.2.

Similar to the Langmuir and Freundlich equations, the inverted Elovich equation given by Eq. (9) can be fitted to adsorption data using a conventional nonlinear regression procedure to minimize the SSR. The Lambert W function is available in several software packages such as MATLAB, Maple, Mathematica, and Mathcad, but not Excel. Highly accurate analytical approximations can be used to evaluate the Lambert W function [42], e.g., in Excel. For numerical computations, a Fortran routine is also available [43].

The loading-explicit Elovich equation, Eq. (9), was fitted to the sulfadiazine adsorption data (case 1) using Mathematica. The commands used were `NonlinearModelFit` and

ProductLog/LambertW. The loading-explicit Elovich equation [Eq. (9)] was found to give identical parameter estimates to those produced by the loading-implicit Elovich equation [Eq. (7)].

Fig. 6 shows the fits of the nonlinear Elovich [Eq. (7)], Langmuir, and Freundlich equations to the q versus c data depicted in Fig. 5A (case 1, sulfadiazine). It is at once evident that all three isotherms can capture the overall shape of the experimental data. According to the R^2 scores, the Langmuir fit is the least accurate ($R^2 = 0.978$), but it is still a huge improvement over the q versus c curve calculated using the parameter estimates produced by the linearized Langmuir fit (Fig. 5A, $R^2 = 0.414$). With an R^2 value of 0.996, the Elovich equation is the best performing model.

It should be noted that the q versus c curve calculated using the parameter estimates obtained by the linearized Elovich fit (Fig. 5A, $R^2 = 0.992$) is only slightly inferior to the nonlinear Elovich fit plotted in Fig. 6. This may be due to the fact that the minimum of SSR is ill-defined, as shown in Fig. 7, so that several combinations of parameters can give a good fit. It is a consequence of (a) the relatively low number of observations and (b) the dispersion of the points at the highest concentrations. Of course, it is not a general property of nonlinear regression.

The result of Fig. 6 should put the final nail in the coffin of the claim that the Elovich equation is vastly inferior to the Langmuir and Freundlich equations. The Elovich equation is equally competitive against the Langmuir and Freundlich equations in the nonlinear correlation of the q versus c data depicted in Figs. 5B–5D (not shown). Table 3 summarizes the parameter estimates, their standard errors, and R^2 scores for the isotherms plotted in Fig. 6. Note that the estimates of the Langmuir parameters produced by the nonlinear fit (Table 3) are much different from those obtained by the linear fit of Eq. (13) (Table 2, case 1). Although the deficiencies of Eq. (13) are well documented in the literature, it can give reliable estimates of

the Langmuir parameters if due attention is given to weighting [44]. Indeed, weighted linear regression based on all linear versions of the Langmuir isotherm will provide parameter estimates close to those produced by nonlinear regression [44].

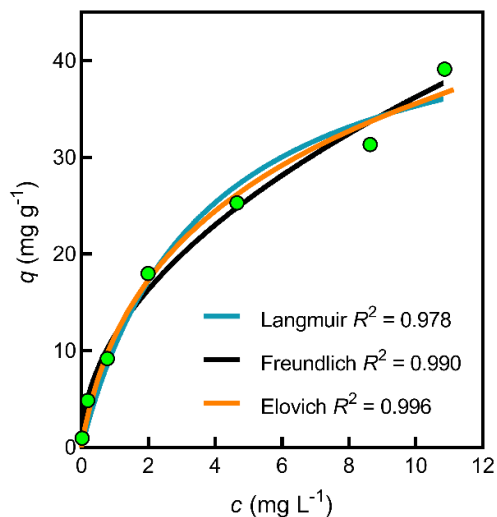


Fig. 6. Nonlinear fits of the Langmuir, Freundlich, and loading-implicit Elovich equations to sulfadiazine adsorption data [15].

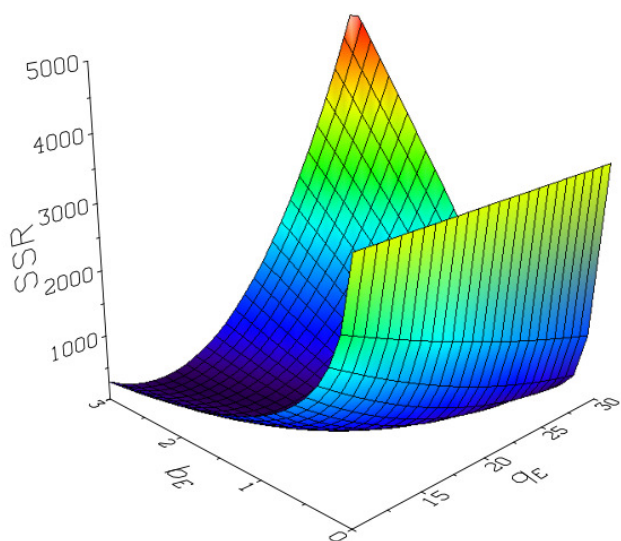


Fig. 7. 3D plot of the sum of squared residuals (SSR) as a function of the parameters q_E and b_E for the nonlinear least-squares fit of the Elovich equation to sulfadiazine adsorption data [15].

Table 3. Fitted parameters, their standard errors, and R^2 values for the nonlinear fits plotted in Fig. 6. ^a

Isotherm	Parameter	Standard error	R^2
Elovich, Eq. (7)	$q_E = 20.60$	3.44	0.996
	$b_E = 0.97$	0.39	
Langmuir, Eq. (11)	$q_m = 47.96$	5.07	0.978
	$b_L = 0.28$	0.08	
Freundlich, Eq. (12)	$n_F = 0.50$	0.04	0.990
	$K_F = 11.57$	0.88	

^a q_E, q_m (mg g^{-1}); b_E, b_L (L mg^{-1}); n_F (-); K_F ($\text{L}^{n_F} \text{mg}^{(1-n_F)} \text{g}^{-1}$).

3.5. Evaluation of energy distribution

If the adsorbent is heterogeneous, the parameter b_E is statistically distributed among the various binding sites. The specific $b_{E,fit}$ value determined by nonlinear regression defines the apparent dissociation constant $K = 1/b_{E,fit}$. K is expressed in mol L^{-1} , assuming a standard state concentration $C^0 = 1$ M. Eqs. (17) and (18) define the adsorption free energies E_0 and E , where R is the gas constant and T is the absolute temperature. Eq. (19) defines the nondimensional variable ε .

$$E_0 = RT \ln(K) \quad (17)$$

$$E = -RT \ln(b_E) \quad (18)$$

$$\varepsilon = \frac{E - E_0}{RT} = -\ln(Kb_E) \quad (19)$$

The probability density function (p.d.f.) of the random variable ε can be computed from the ‘‘Langmuir–Elovich’’ isotherm by the ‘‘condensation approximation’’ method, as described in Appendix A. The final expression is given by Eq. (20).

$$f_\varepsilon(\varepsilon) = \frac{LW [\exp(-\varepsilon)]}{\{1 + LW [\exp(-\varepsilon)]\}^2 \{1 + W [\exp(-\varepsilon)]\}} \quad (20)$$

As shown in Appendix B, the location of the mode of the distribution, i.e., the maximum density, is given by Eq. (21), where w_{max} is defined by Eq. (22).

$$\varepsilon_{max} = -\ln(w_{max}) - w_{max} \quad (21)$$

$$w_{max} = \frac{1}{4} \left(\sqrt{1 + \frac{8}{L}} - 1 \right) \quad (22)$$

The curve is limited by two asymptotic distributions: a Pareto power law at the highest affinities and an exponential distribution at the lowest affinities, with densities of $1/(L\varepsilon^2)$ and $L\exp(-\varepsilon)$, respectively (Appendix C).

The p.d.f. of the random variable E is obtained by equating the probabilities:

$$|f_E(E) dE| = |f_\varepsilon(\varepsilon) d\varepsilon| \quad (23)$$

Hence:

$$f_E(E) = f_\varepsilon(\varepsilon) \frac{d\varepsilon}{dE} = \frac{f_\varepsilon(\varepsilon)}{RT} \quad (24)$$

The maximum is located at:

$$E_{max} = E_0 + RT\varepsilon_{max} = RT \left[\ln(K) + \varepsilon_{max} \right] \quad (25)$$

As an example, data for the adsorption of tyrosine on activated carbon at pH 4 and 20 °C were taken from the work of Dusart et al. [29]. The Langmuir–Elovich isotherm was fitted by simulated annealing [45], using the computer program written by Barry et al. [43] to compute the Lambert W function. The fitted parameters are $q_E = 1.09 \text{ mmol g}^{-1}$, $L = 0.36$, and $b_{E,fit} = 42.8 \text{ L mmol}^{-1} = 42.8 \times 10^3 \text{ L mol}^{-1}$. From the preceding values the following parameters can be calculated: $q_m = q_E/L \approx 3 \text{ mmol g}^{-1}$, $K = 1/b_{E,fit} \approx 2.34 \times 10^{-5} \text{ M}$, and $E_0 = RT\ln(K) \approx -26 \text{ kJ mol}^{-1}$. Fig. 8 shows the fitted curve and the related energy distribution. The mode of the distribution (i.e., the most probable energy) is located at $E_{max} \approx -28 \text{ kJ mol}^{-1}$.

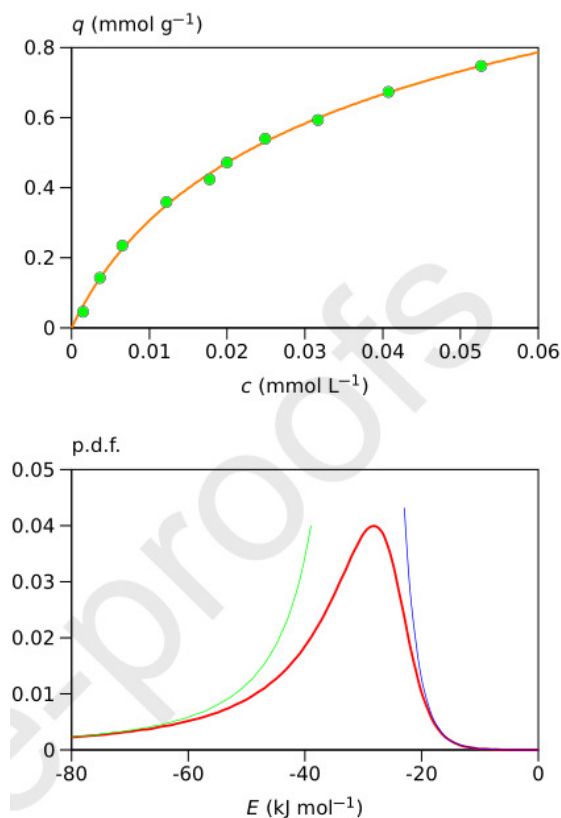


Fig. 8. Adsorption of tyrosine on activated carbon at pH 4 [29]. Upper panel: nonlinear least-squares fit of the Langmuir–Elovich isotherm. Lower panel: energy distribution (red) and its two limiting distributions: Pareto (green) and exponential (blue).

4. Conclusions

Arising from this study, the pertinent points relating to the Elovich equation are the following:

- Many published reports have erroneously claimed that the Elovich equation is much inferior to the Langmuir or Freundlich equation in correlating adsorption equilibrium data. This mistaken conclusion stems from the questionable practice of evaluating and ranking linearized versions of the three isotherms.
- When the parameter estimates of the linear fits are used to predict q versus c data trends, the performance of the Elovich equation is noticeably better than that of the Langmuir

equation and comparable to that of the Freundlich equation. These results reveal that the Elovich equation is highly competitive against the Langmuir or Freundlich equation in data correlation. Therefore, isotherms should be ranked according to how well they describe q versus c data trends.

- Comparison of the nonlinear forms of the three isotherms further debunks the notion that the Elovich equation cannot fit adsorption data well. However, there is a somewhat significant difficulty in applying the nonlinear Elovich equation to experimental data: it is implicit in adsorbed phase concentration. In this work, two practical methods have been proposed to deal with the loading-implicit Elovich equation in nonlinear data fitting.
- The functional form of the Elovich equation is not appropriate for the derivation of a physically meaningful energy distribution. A modified form, called the “Langmuir–Elovich isotherm,” has been successfully introduced to evaluate the energy distribution of heterogeneous surfaces.

Appendix A. Energy distribution

The “condensation approximation” [46] assumes that the cumulative density function (c.d.f.) $F_{b_E}(b_E)$ of the random variable b_E has the same form as the isotherm, as shown in Eq. (A.1), where K is the apparent dissociation constant.

$$F_{b_E}(b_E) = \frac{LW(Kb_E)}{1 + LW(Kb_E)} \quad (\text{A.1})$$

The derivative of the Lambert W function is given by Eq. (A.2) [38].

$$\frac{dW(x)}{dx} = \frac{1}{x} \frac{W(x)}{1 + W(x)} \quad (\text{A.2})$$

The probability density function (p.d.f.) of b_E is $f_{b_E}(b_E) = dF_{b_E}(b_E)/db_E$, so:

$$f_{b_E}(b_E) = \frac{1}{b_E} \frac{LW(Kb_E)}{[1+LW(Kb_E)]^2 [1+W(Kb_E)]} \quad (\text{A.3})$$

We get the p.d.f. of the random variable ε [defined by Eq. (19)] by equating the probabilities:

$$|f_\varepsilon(\varepsilon)d\varepsilon| = |f_{b_E}(b_E)db_E| \quad (\text{A.4})$$

Hence, $f_\varepsilon(\varepsilon) = b_E f_{b_E}(b_E)$, so:

$$f_\varepsilon(\varepsilon) = \frac{LW(Kb_E)}{[1+LW(Kb_E)]^2 [1+W(Kb_E)]} \quad (\text{A.5})$$

Since $Kb_E = \exp(-\varepsilon)$ we obtain Eq. (20).

Appendix B. Coordinates of maximum

Setting $w = W[\exp(-\varepsilon)]$ and derivating Eq. (20) with respect to ε , we obtain:

$$f_\varepsilon(\varepsilon) = \frac{Lw}{(1+Lw)^2(1+w)} \quad (\text{B.1})$$

$$\frac{df_\varepsilon(\varepsilon)}{d\varepsilon} = \frac{Lw(2Lw^2 + Lw - 1)}{(1+Lw)^3(1+w)^3} \quad (\text{B.2})$$

The derivative is null when $2Lw^2 + Lw - 1 = 0$. From the positive root w_{max} [Eq. (22)],

we get the abscissa of the mode (maximum) of the distribution:

$$w_{max} = W[\exp(-\varepsilon_{max})] \quad (\text{B.3})$$

$$\varepsilon_{max} = -\ln w_{max} - w_{max} \quad (\text{B.4})$$

Appendix C. Asymptotic distributions

The behavior of the energy distribution for the highest or lowest affinities, i.e., when $\varepsilon \rightarrow -\infty$ or $+\infty$, respectively, can be deduced from the properties of the Lambert W function. In what follows, $N(a)$ denotes “the neighborhood of a ”.

We start with the relationship:

$$W(x) + \ln[W(x)] = \ln(x) \quad (\text{C.1})$$

According to the work of Corless et al. [38], Eq. (C.1) leads to Eq. (C.2) at $N(+\infty)$, where the notation $o[\ln(x)]$ indicates that $\ln[\ln(x)]/\ln(x) \rightarrow 0$ when $x \rightarrow +\infty$.

$$W(x) = \ln(x) + \ln[\ln(x)] + o[\ln(x)] \quad (\text{C.2})$$

For the highest affinities, $\varepsilon \rightarrow -\infty$, which leads to Eq. (C.3) at $N(-\infty)$.

$$W[\exp(-\varepsilon)] \approx \ln[\exp(-\varepsilon)] = -\varepsilon \quad (\text{C.3})$$

The p.d.f. becomes Eq. (C.4) at $N(-\infty)$.

$$f_\varepsilon(\varepsilon) \approx \frac{-L\varepsilon}{(1-L\varepsilon)^2(1-\varepsilon)} \quad (\text{C.4})$$

Of course, if $\varepsilon \rightarrow -\infty$, $-\varepsilon \gg 1$ and $-L\varepsilon \gg 1$, so the p.d.f. reduces to Eq. (C.5) at $N(-\infty)$.

$$f_\varepsilon(\varepsilon) \approx \frac{1}{L\varepsilon^2} \quad (\text{C.5})$$

For the lowest affinities, $\varepsilon \rightarrow +\infty$ and $x = \exp(-\varepsilon) \rightarrow 0$. We use the relationship given by Eq. (C.6) at $N(0)$.

$$W(x) \approx x \quad (\text{C.6})$$

So, at $N(+\infty)$, the p.d.f. becomes Eq. (C.7).

$$f_\varepsilon(\varepsilon) \approx \frac{L \exp(-\varepsilon)}{[1 + L \exp(-\varepsilon)]^2 [1 + \exp(-\varepsilon)]} \quad (\text{C.7})$$

Eq. (C.7) reduces to Eq. (C.8) at $N(+\infty)$.

$$f_{\varepsilon}(\varepsilon) \approx L \exp(-\varepsilon) \quad (\text{C.8})$$

So, we have a Pareto power law distribution at the highest affinities and an exponential distribution at the lowest affinities.

CRedit authorship contribution statement

All authors contributed equally to this work.

Declaration of competing interest

The authors declare no competing financial interest.

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