

Discussion

Comment on “Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite”

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Abstract

This letter discusses the discrepancies in thermodynamic studies in a recent article by Boubberka et al. Also presented is the significance of the separation factor R_L used to express the essential characteristics of Langmuir isotherm. In addition, the incorrect forms of the two kinetics rate equations, the pseudo-first-order and pseudo-second-order equations used by the authors, are also mentioned.

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Recently, Boubberka et al. published an article entitled “Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite” in *Journal of Hazardous Material* [1], which studied the adsorption of a synthetic dye, Supranol Yellow 4GL, onto Cr-intercalated montmorillonite. There is no doubt that their study is very informative and useful to researchers interested in this field. However, it has come to our attention that several possible errors have been found in their article. We will discuss these issues below.

First of all, in Section 3.4 “Effect of temperature”, thermodynamic parameters, including the enthalpy changes ΔH° , entropy change ΔS° and Gibbs free energy changes ΔG° , were determined for the adsorption of Supranol Yellow 4GL onto Cr-intercalated montmorillonite. However, the results given by Boubberka et al. seem to be questionable. The following equations were adopted for calculation:

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

The values of ΔH° , ΔS° and ΔG° calculated by the authors are displayed in Table 1. We can verify these results by substitut-

ing the values of ΔH° and ΔS° into Eq. (2). It can be found that the magnitude of ΔG° obtained in this way is abnormally larger than that given by the authors. Thus, we think that there may exist some errors in Boubberka et al.’s experimental procedures or data processing.

According to the authors’ statement, the values of ΔH° and ΔS° were determined from the slope and intercept of the Van’t Hoff plot of $\log K_d$ versus $1/T$ (Eq. (1)), while those of ΔG° were calculated using Eq. (2). In order to find out the possible reasons for these discrepancies, a linear regression analysis was performed based on the experimental data. The values of $\log K_d$ and $1/T$ are shown in Table 2 and the plot of $\log K_d$ versus $1/T$ should give a straight line. The values of ΔH° and ΔS° together with the linear equation determined by least squares fit of the experimental data and the corresponding regression coefficients (R^2) are shown in Table 2. It is observed that the value of ΔS° is actually negative; whereas, it might be a little difficult to attribute this to a printing mistake, as the authors presented in Section 3.4 that “the positive value of ΔS° shows increased randomness at the solid-solution interface”. It appears that the authors have drawn a wrong conclusion from a wrong value. We would like to suggest Boubberka et al. to recalculate the thermodynamic parameters and give a reasonable explanation for the interaction between Supranol Yellow 4GL and Cr-intercalated montmorillonite.

Secondly, in Section 3.2 “Effect of initial concentration”, Boubberka et al. used the separation factor R_L to express the

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Table 1
Thermodynamic parameters given by the authors

T (K)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)
283			-14.43
298	-43.560	98.891	-13.275
313			-12.30

Table 2
Results of linear fit of relevant experimental data

Temp. (K)	K_d (cm ³ /g)	$\log K_d$	$1/T$ (10 ⁻³ K ⁻¹)	Linear fit of experimental data
283	735.622	2.867	3.534	$\log K_d = -5.15799$ $+ 2.27248 \times 10^3/T$
298	302.44	2.481	3.356	
313	124.721	2.096	3.195	

ΔH° (kJ/mol)	ΔS° (J/mol K)	R^2
-43.511	-98.761	0.9996

essential characteristics of Langmuir isotherm. The definition of R_L was stated as follows:

$$R_L = \frac{1}{1 + bq_{\max}C_0} \quad (3)$$

We would like to point out that the expression above is not correct, although the authors cited Hall's paper [2] as reference. In fact, this expression is rarely observed in previous literature. R_L is a dimensionless constant, but the multiplication of b (l/mg), q_{\max} (mg/g) and C_0 (mg/l) could not give a dimensionless result. The separation factor was put forward by Hall et al. [2]. The right form of R_L as reported in the original paper is given as:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant and C_0 is the initial concentration of the adsorbate. The value of R_L decreases with increase of b and with increase of initial concentration of the adsorbate.

To address this issue, we performed a general analysis of the significance of the separation factor R_L . The Langmuir equation can be expressed as follows [2]:

$$\frac{q^*}{Q_m} = \frac{bC}{1 + bC} \quad (5)$$

Accordingly, the equilibrium between the saturation concentration q_0^* and the feed concentration C_0 can be presented as:

$$\frac{q_0^*}{Q_m} = \frac{bC_0}{1 + bC_0} \quad (6)$$

When Eqs. (5) and (6) are combined, one gets the following expression:

$$\begin{aligned} \frac{q^*}{q_0^*} &= \frac{C(1 + bC_0)}{C_0(1 + bC)} \\ &= \frac{C}{C_0} \frac{1 + bC_0}{1 + bC_0(C/C_0)} = \frac{C}{C_0} \frac{1 + bC_0}{(1 + bC_0)C/C_0} \\ &= \frac{C}{C_0} \frac{1}{1/(1 + bC_0) + [(1 - 1/(1 + bC_0))C/C_0]} \end{aligned} \quad (7)$$

when substituting Eq. (4) into the expression above, a dimensionless form of the Langmuir equation can be derived solely in terms of separation factor as follows [2]:

$$Y = \frac{X}{R_L + (1 - R_L)X} \quad (8)$$

where X is equal to C/C_0 and Y is equal to q/q_0 . Correspondingly, R_L related to the dimensionless concentrations can be solved by the following expression [2]:

$$R_L = \frac{X(1 - Y)}{Y(1 - X)} \quad (9)$$

The separation factor is commonly adopted as a measure of the adsorbent capacity used. For favorable adsorption, the value of R_L should be within 0 to 1, while $R_L = 0$, $R_L = 1$ and $R_L > 1$, respectively, describe irreversible, linear and unfavorable adsorption. Hence, we propose that the authors recalculate the separation factor using the right equation.

In addition, the authors wrongly expressed the pseudo-first-order equation and pseudo-second-order equation in Section 3.1. The correct forms of them should be written as follows, respectively [3–5]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t \quad (11)$$

We suggest that the authors check back their paper and rectify the possible errors caused by the problematic equations.

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