THEORETICAL APPROACH TO THE FREUNDLICH MODEL AND THERMODYNAMIC PARAMETER INVESTIGATION

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Abstract

In this work, it was proposed a theoretical model which leads to the traditional Freundlich model. The model was fitted to 70 isotherms and compared with results obtained from the Langmuir fitting. It was found that the Freundlich model best describes ($R^2 > 0.95$) the H2 and L1 type isotherm, according to the Giles classification. The natural logarithm of the equilibrium constant based on the Freundlich model was found to range from 6.3 to 20.8, while for the Langmuir it ranges from 6.4 to 15. Both models were able to predict the thermodynamic nature of 85% dataset. The average standard Gibb's free energy difference between both models was found 6.39 kJ mol^{-1}. The estimated standard entropy and enthalpy tend to be higher when estimated from the Langmuir model than the Freundlich. Overall, this work indicates that the Freundlich model can be used for the determination of thermodynamic parameters.

Keywords: adsorption, modeling, isotherm, thermodynamic parameters ;

1. Introduction

The Freundlich model is one of the most applied models in the adsorption field, lagging after the Langmuir model. It was originally developed to investigate adsorption systems involving coal and organic acids [1]. However, although the model may have described the original system and many others, it still lacks proper theory. According to the reference text, the Freundlich model "lacks theoretical background" or "it is empirical only" [2]. In other cases, the Freundlich model is related to heterogeneous systems, meaning that the system energies are not homogeneously distributed [3]. Besides that, the Freundlich model still cannot be employed in determining thermodynamic parameters. Since according to modern methods, the Freundlich constant is not valid for the estimation method [4]. This is another major problem since 20 thousand articles (Web of Science result) have employed the model for describing the adsorption isotherms without reliable determination of the thermodynamic parameters. In this work, the Freundlich model is tackled from a theoretical point of view and further application in the determination of thermodynamic parameters is explored and compared to other methods

2. Model proposal

The following hypotheses were taken into consideration: i) rate adsorption follows fractal reaction and depends on the number of sites with higher affinity, ii) the rate of desorption depends on the adsorbed molecules, and iii) quasi-theoretical and experimental adsorption capacities are approximately equal ($q_{quasi} \approx q_{exp}$). The following kinetics was chosen to describe the adsorption:

$$A + mS \rightarrow AS_m \qquad (1)$$
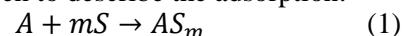
Where A is the adsorbate, m is the number of sites with higher affinity, and AS_m corresponds to the A molecules adsorbed on m occupied sites with higher affinity. The rate of adsorption and desorption can be written as follows:

$$d\theta/dt = k_a C M \theta^m \qquad (2)$$
$$d\theta/dt = -k_d M \theta \qquad (3)$$

Where θ is the coverage (q/q_{max}), t is the time, k_a is the adsorption constant, C is adsorbate concentration, M is the number of available sites, θ^m is the fraction covered, k_d is the desorption constant. At the equilibrium, the following equation is obtained:

$$k_a C_e M \theta^m = k_d M \theta \tag{4}$$
$$(k_a/k_d)C_e = \theta^{m-1} \tag{5}$$

The exponent m-1 and k_a/k_d are properly exchanged to n and K, respectively:

$$\theta^n = KC_e \tag{6}$$

Taking the root of n:

$$\theta = K^{1/n} C_e^{1/n} \tag{7}$$

Considering the nature of the root function, does not reach the equilibrium. It adopted a quasi-adsorption capacity at equilibrium (q_{quasi}), which according to the hypothesis is close to the maximum experimental value ($q_{quasi} \approx q_{max,exp}$). That, the coverage fraction can be calculated according to Equation 8:

$$\theta = q_e/q_{m,exp} \tag{8}$$

Last, the term $K^{1/n}$ is equivalent to the K_F which corresponds to the Freundlich model.

$$q_e = K_F C_e^{1/n} \tag{9}$$
$$K = (K_F)^n \tag{10}$$

3. Thermodynamic estimation

The current estimation method relies on the determination of the equilibrium constant ($K_{eq}^°$) according to the following [4]:

$$K_{eq}^° = \left(K \times M_W \times C_A^°\right)/\gamma_A \tag{11}$$

Where K is the best-fitted model constant (mg L^{-1}), M_w is the molecular weight (mg mol^{-1}), $C_a^°$ is the adsorbate standard concentration (1 mol L^{-1}), and γ_A is the adsorbate activity coefficient (unity, dimensionless). From the equilibrium constant and through the application combined Van't Hoff and Gibb's free energy

$$\Delta G^° = -RTln\left(K_{eq}^°\right) \tag{12}$$
$$ln\left(K_{eq}^°\right) = R\left(\Delta H^°/T + \Delta S^°\right) \tag{13}$$

Where, $\Delta G°$ is the standard Gibbs free energy (kJ mol^{-1}), R is the ideal gas constant (8.31×10^{-4} kJ mol^{-1} K^{-1}), T is the temperature (K), $\Delta H°$ is the standard enthalpy (kJ mol^{-1}) and $\Delta S°$ is the standard entropy (kJ mol^{-1} K^{-1}),

4. Experimental data

Aiming to validate the model and the respective thermodynamic parameters, large experimental data were acquired from the National Institute of Standards and Technology Data Resources for Adsorption Science and Technology (NIST/ARPA-E). From the 3184 results (search conditions: experimental, min temperature 280 K and maximum temperature 328 K), 20 works were separated for this study. Corresponding to 70 isotherm data It should be taken into consideration that: i) only liquid adsorption was selected; ii) only results with 3 temperatures or more were selected; iii) unfavorable isotherms were also avoided.

5. Isotherm fitting and statistical evaluation

Besides the Freundlich model, the Langmuir model was employed as a comparison model for each data group. The coefficient of correlation was used as a statistical indicator. All fitting and plots were done by Originlab pro-2016.

6. RESULTS AND DISCUSSION

Considering the number of isotherms analyzed and Giles classification, it was found that 35.2% corresponds to the H2 type, with 2.81% of these isotherms do not exhibit the plateau [5]. Regarding the L1, 23.94% of the data corresponds to this type. Last, 40.84% corresponds to the L2 shape with 18.30% does not present the plateau. Regarding the performance of each model (Figure 1), it was found that for this database the Langmuir tends to represent 42 of the isotherm groups while the Freundlich model better represents 28.

The latter is better fitted to describe H2, L1 and L2 without the plateau. According to the Giles original classification, the H type is related with strong interaction between the adsorbate and adsorbent, which is in agreement with the proposed theory. Furthermore, the high affinity between the adsorbate and adsorbent can occur in L1 and L2 types. Another important comparison is the K_{eq}^0 values according to each model. In this case, it was chosen to evaluate through $ln(K_{eq}^0)$. For this data was classified according to the type and R^2.
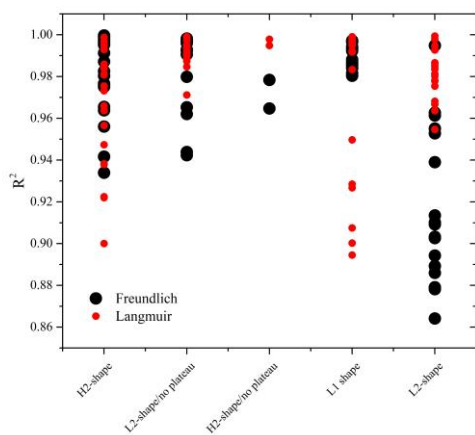
Fig. 1. Correlation factor according to the model and isotherm type.

Figure 2. a shows that the Freundlich model tends to cluster at the H2 and L1 type, with values ranging from 6.3 to 20.8. On the other hand, the equilibrium values obtained from the Langmuir model (Figure 3b) indicate that the model best describes the L2 with no plateau, with values ranging from 6.4 to 15. These results sound contradictory since it is expected that the Langmuir model to describe L2 with a plateau better than without. These results are most related to the data employed, meaning that some experimental results may not be fitted to any of the models tested.

Regarding the thermodynamical nature of the systems, it was found that 13 systems are endothermic, 5 are exothermic and 2 are a mixture of both (adsorption capacity oscillates with the temperature). Both models failed to predict the thermodynamic nature of the 3 data sets, being 2 the same group, indicating that the model cannot describe this pattern. Disregarding the failed cases, the estimated standard Gibbs free energy has an absolute difference of 6.39 kJ mol^{-1} between the two models. This indicates that in most cases the Freundlich model was able to keep up with the Langmuir model. The standard Gibbs free energy according to the data set and the R2 (Eq 13 fitting) is given in Figure 3. The $\Delta G°$ tends to be more clustered from the Freundlich model, while the Langmuir tends to be scattered more. This is

directly related to the temperature effect, which indicates that the Langmuir constant is more sensible to the system temperature. Besides that, when the R^2 is above 0.97 the parameters obtained from the Freundlich correspond to 12 isotherms, while the Langmuir corresponds to 9.
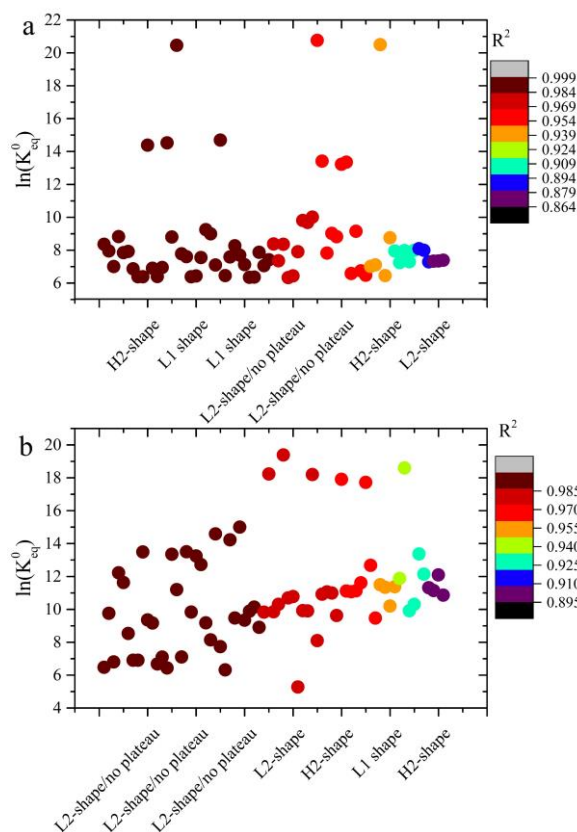

Fig. 2. Equilibrium constant natural logarithm according to the R^2, isotherm type, and model: (a) Freundlich, and (b) Langmuir.

Last, the trend $\Delta S°$ vs $\Delta H°$ is shown in Figure 4. It was found that the thermodynamic values obtained from Langmuir and Freundlich models tend to follow linear trends, with smaller deviations for the latter one. In addition, it should be noted that in most cases the $\Delta S°$ and $\Delta H°$ are smaller for the Freundlich in comparison with the Langmuir. According to Asnin and Collaborators [6], the Freundlich model can be employed for the determination of thermodynamic quantities at lower concentrations, however, the authors did not specify the range to which these small concentrations belong. Thus the differences regarding the linearity

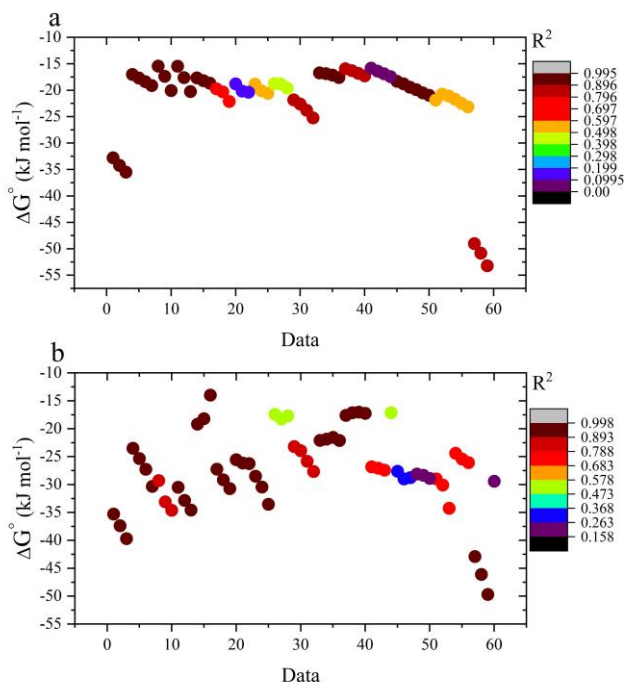and magnitude can be related to the experimental data.

Fig. 3. Equilibrium constant natural logarithm according to the R^2, isotherm type, and model: (a) Freundlich, and (b) Langmuir.
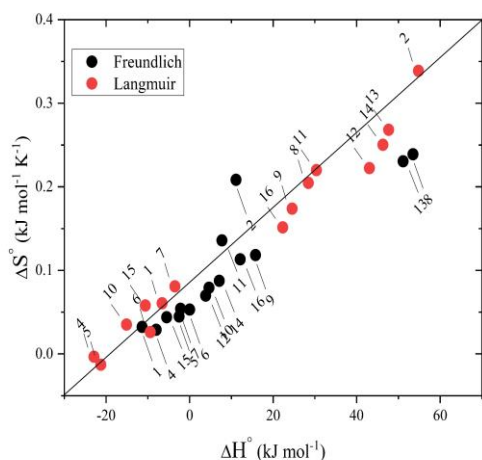

Fig. 4. Equilibrium constant natural logarithm according to the R^2, isotherm type, and model: (a) Freundlich, and (b) Langmuir.

6. CONCLUSION

In this work, a theoretical background was proposed for the Freundlich model. This enables the estimation of the Freundlich parameter in units of mg L^{-1}. Which are in agreement with the current method for the determination of the thermodynamic parameters. It was found that the Freundlich model tends to describe the H2 isotherm type equally or better than the Langmuir model. It was also found that the equilibrium constant obtained from the Freundlich model can be employed in the determination of thermodynamic parameters. Overall, these results indicate that the Freundlich model does correlate with "some theory". Further investigation regarding the hypothesis assumed and expansion of the experimental data are needed to validate the model without leaving any doubt.

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