Reparameterization and estimation of Freundlich model parameters for CO_2 adsorption on hydrotalcite

Ramon Vinícius Santos de Aquino[a,*], José Luciano Soares[a], Alisson Lopes Freire[a], Bruno Francisco Oechsler[a], Regina de Fátima Peralta Muniz Moreira[a]

[a] Department of Chemical and Food Engineering, Rua do Biotério Central, s/n, Florianópolis 88040-900, Brazil

Abstract

In this study, CO_2 adsorption equilibrium parameters were estimated using Particle Swarm Optimization (PSO) before and after reparameterization of the Freundlich model. Experimental data was obtained from an isotherm study of CO_2 adsorbed on hydrotalcite. The Langmuir and Freundlich models were initially compared, with only the Freundlich model being suitable to represent the experimental data according to the Chi-squared test. The Freundlich model was reparameterized to establish independence between the estimated parameters, k_F and n, by using a reference value. The confidence region between the parameters shifted to an elliptical form, and the correlation coefficient decreased considerably after reparameterization, indicating that the estimation became independent and statistically significant.

Keywords: correlation; hydrotalcite; particle swarm optimization

1. Introduction

Carbon dioxide is considered the greenhouse gas that contributes most to global warming. The urgent need to reduce CO_2 emissions persists, despite the continued increase of this component in atmospherfrom sources such as thermoelectric power plants, biogas production, and oil refineries [1].

Consequently, clean and efficient technologies for mitigating CO_2 have been extensively studied, whether for storage or utilization in other processes. Adsorption presents itself as a well-established technique for this purpose, as it can employ highly efficient solid materials and has a high degree of industrial maturity [2].

The adsorption process involves the mass transfer of a component of interest from the gas phase (adsorbate) to a porous solid (adsorbent). Adsorbents with high porosity and specific surface area can enhance the interactions at the solid-gas interface, leading to a higher adsorption capacity [3].

Anion clays, particularly hydrotalcites, have emerged as promising adsorbents in recent years. These materials have a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{2+}(A^{n-})_{x/n}.mH_2O$, where M^{2+} and M^{3+} are typically represented by metals such as Mg and Al, and A represents the charge-compensating anion, usually carbonate (CO_3^{2-}). Hydrotalcites offer advantages such as low cost, high adsorption capacity, and easy regeneration [2].

A crucial aspect of adsorption is the equilibrium at the solid-gas interface. At constant temperature, after a certain time, equilibrium is reached, where the adsorption and desorption rates attain equal values. Isotherms, constructed based on these data, provide valuable insights into the adsorption process.

Langmuir and Freundlich models are the most commonly employed models for adsorption equilibrium data. These models provide valuable insights into the type of interaction and reversibility of the adsorption process. The Langmuir model describes monolayer adsorption and is generally suitable for active sites that bind to only one molecule. Freundlich, on the other hand, represents a multilayer process with an exponential distribution of active sites, and is applicable to gas-phase adsorption on heterogeneous surfaces [4].

Conventional adsorption equilibrium models often exhibit high correlation between their parameters, leading to low reliability and significant deviations between model predictions and experimental data. One approach to overcome these challenges in parameter estimation is to renormalize the models using a reference value. This adjustment can improve the minimization of the objective function and substantially reduce the correlation between model parameters [5].

Heuristic methods such as genetic algorithms [6] and particle swarm optimization (PSO) [5] can be applied to more accurately find global minimum values in this type of parameter estimation. The PSO algorithm exhibits excellent performance, requiring less computational effort compared to other heuristic algorithms [7]. Therefore, this type of method can be considered highly interesting for application in adsorption equilibrium models.

In this work, commercial hydrotalcite was used to obtain CO_2 adsorption isotherms. Equilibrium models were applied, followed by reparameterization and parameter estimation using the PSO method.

2. Methodology

Experimental data for this study was obtained by Soares [8]. For the equilibrium isotherm tests, CO_2 (99.998%) was used as adsorbate and He (99.999%) as inert gas, both supplied by Air Liquide, Portugal. The adsorbent used was commercial hydrotalcite (specific surface area of 154 $m^2.g^{-1}$, and porosity of 0.63) in the form of cylindrical pellets (Condea Ouralox, South Africa) with a magnesium oxide content of 30%. The tests were conducted using a thermogravimetric method with a microbalance (CI-Robal, United Kingdom). Approximately 100 mg of adsorbent was heated under vacuum to 500 °C (heating rate of 5 °C/min) and kept at this temperature for 10 hours for activation. Subsequently, the system was cooled to 150°C, the temperature tested in the equilibrium experiments. The amount of CO_2 adsorbed at equilibrium was determined by stabilizing the gas pressure and reading the mass on the microbalance. The equilibrium models tested in this study were Langmuir (Equation 1) and Freundlich (Equation 2).

$$q_e = \frac{q_m . k_L . P}{1 + k_L . P} \tag{1}$$

$$q_e = k_{F.} P^n \tag{2}$$

Where q_e is the equilibrium adsorption capacity ($mmol.g^{-1}$), q_m is the maximum adsorption capacity obtained by the Langmuir model ($mmol.g^{-1}$), P is the adsorbate partial pressure in equilibrium (kPa), n is the heterogeneity factor, and k_L and k_F are the Langmuir and Freundlich equilibrium constants, respectively. For the Freundlich model, a reparameterization technique (Equation 3) [5] was also used to decrease the correlation between parameters, thus making the estimates more significant.

$$q_e = k_{ref} . (P/P_{ref})^n \tag{3}$$

Where k_{ref} is the Freundlich reference constant and P_{ref} is the reference equilibrium pressure after reparameterization. The expressions used for the calculation of k_{ref} and P_{ref} are given in Equations 4 and 5.

$$k_{ref} = k . P_{ref}^n \tag{4}$$

$$P_{ref} = \exp \exp \left[\sum_{i=1}^{NE} q_{e,i}^2 \frac{\ln ln \left(P_i\right)}{\sum_{i=1}^{NE} q_{e,i}^2} \right] \tag{5}$$

Parameter estimation was performed using the ESTIMA [5], which employs a hybrid algorithm combining the heuristic PSO method and the deterministic Gauss-Newton method. For the application of ESTIMA, the integrated Spyder environment, using Python programming, was required. The weighted least squares objective function (F_{obj}) was used (Equation 6).

$$F_{obj} = \sum_{i=1}^{NE} \frac{\left(y_i^e - y_i^m\right)^2}{\sigma_i^2} \tag{6}$$

Where y^e and y^m are the experimental and model-calculated values for the experimental output variable, respectively. NE is the number of experiments and σ^2 is the experimental variance. The chi-squared statistical test determined the model's ability to represent the experimental data adequately. A 95% confidence level was used. The PSO parameters used were the inertial parameter (in the range of 0.95-0.75) and the population parameter (1.5).

3. Results and Discussion

Initially, the parameters of the Langmuir and Freundlich models were estimated using the ESTIMA software, with the Chi-squared test employed to statistically validate the fits. The Chi-squared test results indicated that the Freundlich model exhibited an objective function (F_{obj}) of 10.725, with lower and upper confidence limits of 1.689 and 16.013, respectively. The Langmuir model yielded a significantly higher F_{obj} of 70.995 within the same confidence intervals. The Freundlich model parameters were determined to be $k_F = 0.165$ mmol.g^{-1}.kPa$^{1/n}$ and n = 0.275.

It was observed that the Freundlich model was suitable for representing the experimental data, as the objective function value fell within the test limits. In contrast, the Langmuir model exhibited a much higher objective function value than the upper test limit, rendering it unsuitable for representing the data.

This suggests that multilayers of CO_2 molecules may be formed on the catalyst surface. The value of n below 1 indicates that the adsorbent surface is heterogeneous. As the adsorbate pressure increases, the process tends to become unfavorable because the favorable sites are already occupied.

Figure 1 presents the models fitted to the data. It can be observed that the Freundlich model provides a better fit than the Langmuir model, as statistically predicted by the Chi-squared test.

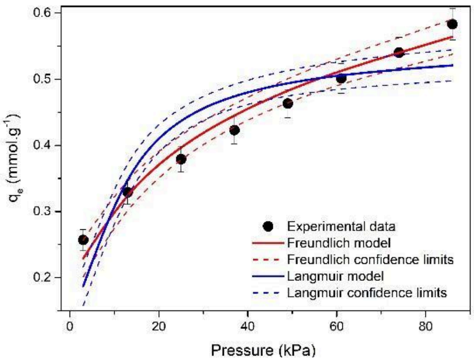

Figure 1. Equilibrium data fitted to the Langmuir and Freundlich model.

Figure 2 shows the confidence region between parameters n and k_F.

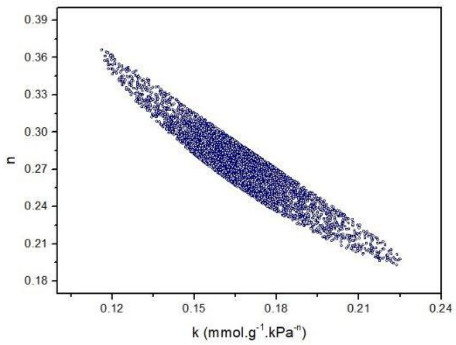

Figure 2. Confidence region of the estimated parameters for the Freundlich model.

The confidence region significantly deviates from an elliptical shape, indicating a high correlation between parameters. This means that they cannot be estimated independently, as evaluated by Borges et al. [9]. Models with a direct analytical solution and simple datasets, such as those in this work, should present confidence regions close to an ellipsoid, in agreement with a normal distribution. However, the high correlation of the power function model parameters prevented this from occurring. This justifies the use of renormalization in this case.

After selecting the Freundlich model, a reparameterization was performed to increase the statistical significance of the estimated parameters. According to Schwaab and Pinto [5], power function models have a high correlation between parameters, therefore, the Freundlich equation was renormalized to a reference value for k_F and P, as shown in Equations 4 and 5 in the methodology section. Since the values of k_{ref} and P_{ref} do not change the response variable, the model fit in this new format was identical to that in Figure 1. Figure 3 shows the confidence region with the model in the reparameterized form.

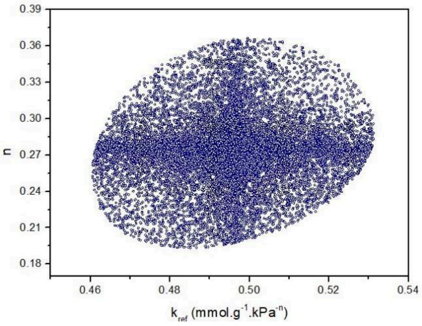

Figure 3. Confidence region of the estimated parameters for the reparameterized Freundlich model.

The high correlation between k_F and n was successfully addressed through model reparameterization. The modified model exhibited statistically significant parameters and an elliptical confidence region, indicating a more reliable parameter estimation. Furthermore, correlation matrices were generated to corroborate these findings. The correlation coefficients for the non-reparameterized and reparameterized models were -0.976 e 0.218, respectively. The coefficients presented above reveal a significant reduction in the absolute correlation between the parameters of the reparameterized model compared to the original model. This suggests that the Freundlich parameters have become nearly independent.

4. Conclusions

This study revealed that the methods used to adjust the adsorption equilibrium data substantially enhanced the accuracy of the Freundlich model parameter estimates following reparameterization. The formation of an elliptical confidence region and an approximately 80% reduction in the absolute value of the correlation coefficient were observed following the reparameterization procedure, rendering the k_F and n parameters independent and statistically significant. This method can be applied to other adsorption models and processes to enhance the quality of the estimated parameters.

References

[1] Suescum-Morales D, Cantador-Fernández D, Jiménez JR, Fernández JM. Mitigation of CO_2 emissions by hydrotalcites of $Mg_3Al\text{-}CO_3$ at 0 °C and high pressure. Applied Clay Science, v. 202, 105950, 2021.

[2] Fernández DC, Morales DS, Jiménez JR, Fernández-Rodriguez JM. Schwaab M, Pinto JC. CO_2 adsorption by organohydrotalcites at low temperatures and high pressure. Chemical Engineering Journal, v. 431, 134324, 2022.

[3] Leng L, Xiong Q, Yang L, Li H, Zhou Y, Zhang W, Jiang S, Li H, Huang H. An overview on engineering the surface area and porosity of biochar. Science of The Total Environment, v. 763, 144204, 2021.

[4] Al-Ghouti M, Da'ana DA. Guidelines for the use and interpretation of adsorption isotherm models: A review. Journal of Hazardous Materials, v. 393, 122383, 2020.

[5] Schwaab M, Pinto JC. Optimum reparameterization of power function models. Chemical Engineering Science, v. 63, n. 18, p. 4631-4635, 2008.

[6] Pajak M, Buchaniec S, Kimijima S, Szmyd J, Brus G. A multiobjective optimization of a catalyst distribution in a methane/steam reforming reactor using a genetic algorithm. International Journal of Hydrgen Energy, v. 46, n. 38, p. 20183-20197, 2021.

[7] Schwaab M, Biscaia EC, Monteiro JL, Pinto JC. Nonlinear parameter estimation through particle swarm optimization. Chemical Engineering Science, v. 63, p. 1542-1552, 2008.

[8] Soares JL. Desenvolvimento de novos adsorventes e processos híbridos em reforma catalítica por vapor de água. 165 p. PhD thesis. Federal University of Santa Catarina, Florianópolis, 2003.

[9] Borges RFO, Oechsler BF, Oliveira BR, Andrade LDR, Calçada LA, Scheid CM, Calado V. Reparametrization of static filtration model of aqueous-based drilling fluids for simultaneous estimation of compressible mudcake parameters. Powder Technology, v. 386, p. 120-135, 2021