ENVIRONMENTAL BIOTECHNOLOGY

ESTIMATION OF PARAMETERS USING BAYESIAN TECHNIQUES IN THE ADSORPTION OF MULTICOMPONENT SYSTEMS

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ABSTRACT

Adsorption is an important process in removing contaminants from drinking water, where different polluting substances are present at the same time. To improve the effectiveness of water treatment systems, it is essential to use models that consider multiple components, such as the Langmuir isotherm, which describes how the amount of adsorbed substance (Q_e) relates to the concentration of the substance in the equilibrium solution (C_e) after adsorption. However, this model does not take into account the interaction between different adsorbents after adsorption. This study focuses on a binary system of cobalt and nickel, using the Markov Chain Monte Carlo Method to estimate parameters. This method is an iterative simulation technique that allows obtaining a sample of the posterior distribution. When comparing the estimated values with the reference values, the method proved to be satisfactory.

Keywords: Isotherm. Langmuir. MCMC. Modeling. Simulation.

1 INTRODUCTION

Adsorption is a crucial phenomenon in the removal of contaminants, especially in the purification of drinking water. Various contaminants, such as arsenic, fluoride, vanadium, chromium, nickel, cadmium, and cobalt, are naturally found in multicomponent mixtures in water. Therefore, the modeling of multicomponent adsorption isotherms has become important for the development of effective water treatment systems. A model, based on the Langmuir isotherm, was developed for multicomponent systems.[1] This model is based on adsorption without competition for the adsorbate's active site. In this work, a binary system, cobalt-nickel, will be studied, each adsorbent has four parameters, and with this, we will estimate these parameters using the Markov Chain Monte Carlo Method through the Metropolis-Hastings algorithm.

2 MATERIAL & METHODS

Extended Langmuir Model.

Based on the Langmuir isotherm, a model for multicomponent systems was developed, according to equation (1).[1]

$$Q_{e,i} = \frac{Q_{máx,i} K_i C_{e,i}}{1 + \sum_{j=1}^{n} K_j C_{e,j}} \tag{1}$$

This model uses the Langmuir isotherm to describe the amount adsorbed $\left(Q_{eq,i}(mg/g)\right)$ per unit mass of adsorbent at equilibrium concentration $\left(C_{eq,i}(mg/L)\right)$. The parameters K_i and $Q_{max,i}$ are derived from the Langmuir isotherm for systems with a single component, being suitable for systems where individual adsorption data fit well to the Langmuir isotherm.[2] However, when the components have molecules of very different sizes, $Q_{max,1}$ does not approach $Q_{max,2}$, resulting in an unsatisfactory fit to the extended Langmuir model.[3,4]

In this model, the interaction between the adsorbates after adsorption is not considered; furthermore, it assumes a homogeneous surface and equal distribution of adsorbed sites for the adsorbents.

Markov Chain Monte Carlo.

Sampling from the posterior distribution using Markov Chain Monte Carlo (MCMC) methods is the most general technique for calculating estimates within the Bayesian framework. The most common MCMC technique is the Metropolis-Hastings algorithm.[5,6,7] The implementation of the Metropolis-Hastings algorithm begins with the selection of a proposed distribution $r\left(\theta^*, \theta^{(t-1)}\right)$ which is used to draw a new candidate state θ^*, given the current state θ^t of the Markov chain. Once the proposal distribution is selected, the Metropolis-Hastings sampling algorithm can be implemented by repeating the following steps:

1. Sample a candidate point θ^* from the proposed distribution $r(\theta^*, \theta^{(t-1)})$.
2. Calculate the acceptance factor:

$$\text{AF} = \min\left[1, \frac{\pi(\theta^*|Y)r(\theta^{(t-1)}, \theta^*)}{\pi(\theta^{(t-1)}|Y)r(\theta^*, \theta^{(t-1)})}\right] \tag{2}$$

3. Generate a random value U which is uniformly distributed on (0,1).
4. If U ≤ AF define $\theta^t = \theta^*$. Otherwise, $\theta^t = \theta^{(t-1)}$.
5. Record the current state.
6. Return to step 1 and repeat until the required posteriori samples are obtained.

Consequently, a sequence is generated to describe the posterior distribution and inference about this distribution is reached from inference on the samples $\{\theta^{(1)}, \theta^{(2)}, \dots, \theta^{(n)}\}$. However, we note that the values of $\theta^{(i)}$ must be ignored until the chain has converged to equilibrium (the burn-in period). In this work the proposal was taken as a random walk in the form:

$$\theta^* = \theta^{(t-1)} + w\theta^{(t-1)}\varepsilon \tag{3}$$

where ε is a random vector with standard normal distribution, that is, $\varepsilon \sim N(0,1)$.

3 RESULTS & DISCUSSION

This study will consider the estimation of four parameters: $Q_{max,Co}$, $Q_{max,Ni}$, K_{Co} and K_{Ni}. Table 1 below presents the reference values as well as statistical metrics for the estimates obtained.

Table 1 Reference values and parameter estimates.

Parameter	Unit	Exact Value	Initial Estimation
$Q_{max,Co}$	mg/g	144,61	289,22
$Q_{max,Ni}$	mg/g	147,21	294,42
K_{Co}	dimensionless	0,0031	0,0062
K_{Ni}	dimensionless	0,0034	0,0068

Finally, Figure 1-2 shows the evolution of the amount of adsorbed adsorbate (Q_e) by the equilibrium adsorbate concentration in the solution after adsorption (C_e), a comparison between experimental and estimated measurements. These quantities are in excellent agreement.
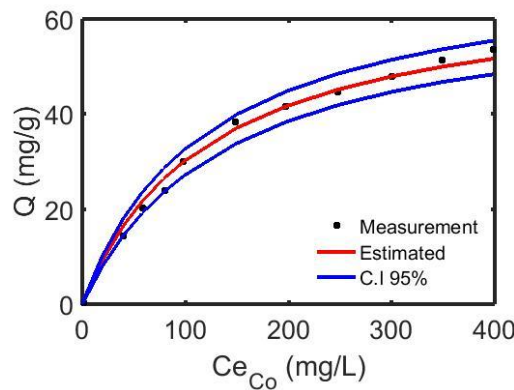
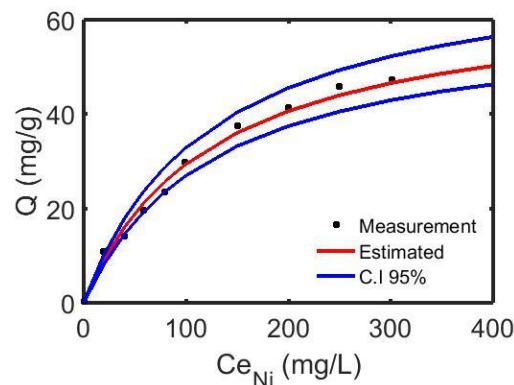**Figure 1** Comparison between experimental and estimated measurements for Cobalt.

Figure 2 Comparison between experimental and estimated measurements for Nickel.

4 CONCLUSION

The Markov Chain Monte Carlo method proved to be robust enough to obtain parameter estimates from the extended Langmuir isotherm model when comparing parameter estimates with reference values. As well as the simulated and experimental isotherm profiles, they showed excellent agreement.

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