BAYESIAN PARAMETER ESTIMATION IN MULTICOMPONENT DRUG ADSORPTION SYSTEMS

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ABSTRACT

The work demonstrates concern regarding the excretion of pharmaceutical products after consumption, highlighting the challenges for their efficient removal, especially in aquatic environments. Given the inefficacy of traditional treatment methods, there is a growing interest in adsorption techniques for removing these compounds. Modeling multicomponent adsorption isotherms has become crucial for creating effective water treatment systems, using a model based on the Langmuir isotherm. The study proposes to analyze a system involving four pharmaceutical elements and using sugarcane bagasse as the adsorbent. The technique called Markov Chain Monte Carlo Method was applied to determine the adsorption parameters, where excellent agreement was observed between the profiles of simulated and experimental isotherms.

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

1 INTRODUCTION

Pharmaceutical products, integral for human and animal health, raise concerns upon excretion due to potential unknown effects on humans and aquatic life[1,2]. Compounds like anti-inflammatories and antibiotics, naturally found in various sources including hospital effluents, pose challenges for efficient removal, prompting interest in techniques such as adsorption for their promising effectiveness3[3,4,5,6]. Multicomponent adsorption isotherm modeling, particularly based on the Langmuir model[7], has become crucial for designing effective water treatment systems, describing how different substances adsorb onto materials without interfering with each other in the same binding space.

This study focuses on analyzing a previously conducted investigation of competitive drug adsorption from multicomponent mixtures using sugarcane bagasse as the adsorbent[8]. The system involves four elements: ciprofloxacin (CPX), sulfamethoxazole (SMX), ibuprofen (IBU), and diclofenac (DCF), each characterized by four specific parameters. Employing the Monte Carlo via Markov Chain Method, specifically the Metropolis-Hastings algorithm, facilitates efficient and precise estimation of these parameters, aiding in understanding the complex dynamics of adsorption in such systems.

2 MATERIAL & METHODS

Extended Langmuir Model.

A model was developed for systems dealing with multiple components, using the Langmuir isotherm as a basis[7]. This model is represented by equation (1).

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

This model employs the Langmuir isotherm to explain the amount of adsorbed substance $\left(Q_{eq,i}(mg/g)\right)$ per unit mass of adsorbent at a given equilibrium concentration $\left(C_{eq,i}(mg/L)\right)$. The parameters K_i and $Q_{max,i}$ are obtained from the Langmuir isotherm for single-component systems and are suitable when individual adsorption data fit well to this isotherm[9]. However, when the components have molecules of vastly different sizes, the maximum adsorption capacity for one component does not resemble the maximum adsorption capacity for another component, resulting in a poor fit to the extended Langmuir model. In this model, no interaction between the adsorbates after adsorption is considered, and it is presumed that the surface is homogeneous, with a uniform distribution of adsorption sites for the adsorbates[10,11].

Markov Chain Monte Carlo.

Data collection of the posterior distribution using Markov Chain Monte Carlo (MCMC) methods is the most widely applied approach for computing estimates within a Bayesian context. The most common MCMC method is the Metropolis-Hastings algorithm[12,13,14].

To implement this algorithm, a proposal distribution $r(\theta^*, \theta^{(t-1)})$ is first chosen, which is used to generate a new candidate state, θ^*, based on the current state of the Markov chain, θ^t. After selecting the proposal distribution, the Metropolis-Hastings algorithm is executed by repeating the following steps:

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

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

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

Thus, a series of numbers is produced to represent the posterior distribution, and understanding this distribution is derived from the analysis of the values contained in these generated numbers $\{\theta^{(1)}, \theta^{(2)}, \ldots, \theta^{(n)}\}$. However, it is important to note that individual values $\theta^{(i)}$ should be disregarded until the data chain has reached a stable equilibrium state, known as the burn-in period. In the context of this study, the approach adopted for generating new values was modeled as a random walk process:

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

Where ε represents a vector of random numbers following a standard normal distribution, that is, each element of ε is randomly selected according to a normal distribution with mean zero and standard deviation equal to one $(\varepsilon \sim N(0,1))$.

3 RESULTS & DISCUSSION

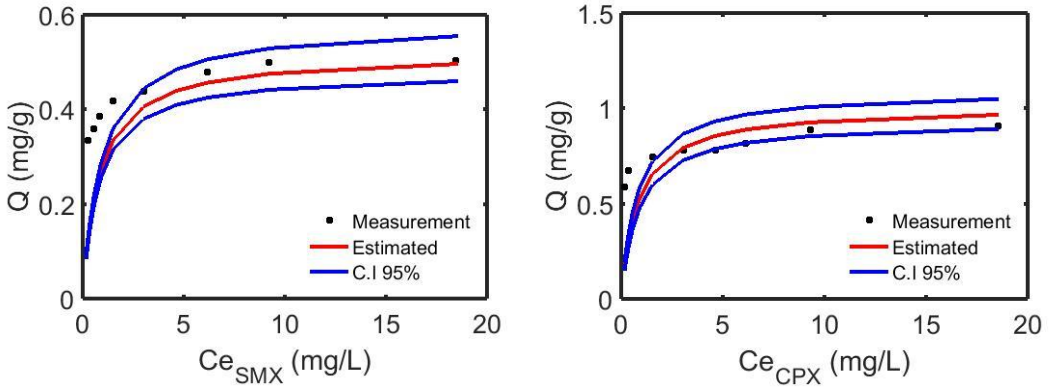
In this study, estimates of eight parameters will be analyzed: $Q_{max,SMX}$, $Q_{max,CPX}$, $Q_{max,DFC}$, $Q_{max,IBU}$, K_{SMX}, K_{CPX}, K_{DFC} and K_{IBU}. Table 1 will display the reference values[8] along with the statistical metrics of the estimates performed.

Table 1 Reference values and parameter estimates.

Parameter	Unit	Reference Value[8]	Initial Estimation	Mean	C. I. 95%
$Q_{max,SMX}$	mg/g	1,43	2,86	4,22	(4,06; 4,28)
$Q_{max,PCX}$	mg/g	2,61	5,22	2,83	(2,02; 4,16)
$Q_{max,DFC}$	mg/g	1,81	3,62	3,81	(2,32; 5,31)
$Q_{max,IBU}$	mg/g	1,62	3,24	2,74	(2,38; 3,30)
K_{SMX}	Dimensionless	0,05	0,10	0,15	(0,14; 0,15)
K_{CPX}	Dimensionless	0,22	0,44	0,45	(0,29; 0,58)
K_{DFC}	Dimensionless	0,24	0,48	0,29	(0,19; 0,45)
K_{IBU}	Dimensionless	0,12	0,24	0,31	(0,23; 0,36)

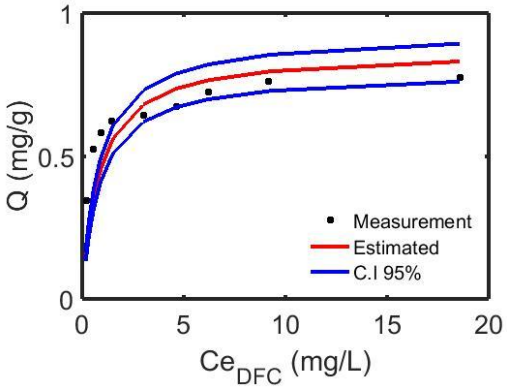
And finally, Figure 1 (a-d) shows a comparison between the experimentally measured values and those estimated of the relationship between the amount of substance adsorbed per unit mass of adsorbent (Q_e) and the concentration of this substance at equilibrium (C_e). The low affinity of SMX with the adsorbate and the difficulty in removing SMX from a multicomponent solution are observed.

Figure 1 Comparison between experimental and estimated measurements.

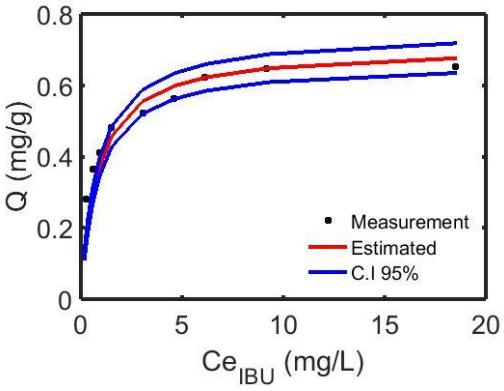


(a) Sulfamethoxazole.

(b) Ciprofloxacin.



(c) Diclofenac.



(d) Ibuprofen.

4 CONCLUSION

The Monte Carlo via Markov Chain method has proven to be quite robust in obtaining estimates of the parameters of the extended Langmuir isotherm model, as evidenced by the comparison of parameter estimates with reference values. Additionally, excellent agreement was observed between the profiles of simulated and experimental isotherms. With the exception of the SMX component, which showed low affinity with the adsorbate, as evidenced by the K_{SMX} constant, both by the reference value[8] and the estimated value.

REFERENCES

1 LOPES, B. C. Effects of photolysis and heterogeneous photocatalysis on the dynamics of drugs present in biologically treated sewage. 2014. Dissertation (Master's in Sanitation, Environment and Water Resources) – Federal University of Minas Gerais, Minas Gerais, Brazil, 2014.

2 HAMDI EL NAJJAR, N.; TOUFFET, A; DEBORDE, M.; JOURNL, R.; LEITNER, K. V. Kinetics of paracetamol oxidation by ozone and hydroxyl radicals, formation of transformation products and toxicity. Separation and Purification Technology, v. 136, p. 137-143, 2014.

3 FRANCO, M. A. E.; CARVALHO, C. B.; BONETTO, M. M.; SOARES, R. P.; FÉRIS, L. A. Removal of amoxicillin from water by adsorption onto activated carbon in batch process and fixed bed column: Kinetics, isotherms, experimental design and breakthrough curves modeling. Journal of Cleaner Production, v. 161, p. 947-956, 2017.

4 PEZOTI, O.; CAZETTA, A. L.; BEDIN, K. C.; SOUZA, L. S.; MARTINS, A. C.; SILVA, T. L.; JÚNIOR, O. O. S.; VISENTAINER, J. V.; ALMEIDA, V. C. NaOH-activated carbon of high surface area produced from guava seeds as a high-efficiency adsorbent for amoxicillin removal: Kinetic, isotherm and thermodynamic studies. Chemical Engineering Journal, v. 288, p. 778-788, 2016.

5 CHAYID, M. A.; AHMED, M. J. Amoxicillin adsorption on microwave prepared activated carbon from Arundo donax Linn: Isotherms, kinetics, and thermodynamics studies. Jornal of Environmental Chemical Engineering, v. 3, p. 1592-1601, 2015.

6 NANAKI, S. G.; KYZAS, G. Z., TZEREME, A.; PAPAGEORGIOU, M.; KOSTOGLOU, M.; BIKIARIS, D. N.; LAMBROPOULOU, D. A. Synthesis and characterization of modified carrageenan microparticles for the removal of pharmaceuticals from aqueous solutions. Colloids Surf. B: Biointerfaces, v. 127, p. 256–265, 2015.

7 MARKHAN, E.C.; BENTON, A.F. The adsorption of gas mixtures by silica. Journal of the American Chemical Society, v. 53, n. 1, p. 497–507, 1931.

8 PEÑAFIEL, M. E.; FLORES, D. Competitive Adsorption of Drugs from a Multi-Component Mixture on Sugarcane Bagasse. *Water* 2023, *15*, 2127.

9 CHOY, K. K. H; PORTER, J. F.; MCKAY, G. Langmuir isotherm models applied to the multicomponent sorption of acid dyes from effluent onto activated carbon. Journal of Chemical and Engineering Data, v. 45, n. 4, p. 575-584, 2000.

10 VALDERRAMA, C.; BÁRIOS, J. I.; FARRAN, A.; CORTINA, J. L. Evaluating binary sorption of phenol/aniline from aqueous solutions onto granular activated carbon and hypercrosslinked polymeric resin (MN200). Water, Air, and Soil Pollution, DOI 10.1007/s11270-009-0266-7 (published 19 November 2009).

11 RUTHVEN, D. M. Principles of adsorption and adsorption processes. New York: Wiley, 1984.

12 GAMERMAN, D., 1997, " Markov Chain Monte Carlo: Stochastic simulation for Bayesian Inference". First ed. London: Chapman & Hall.

13 ORLANDE, H., FUDYM, F., MAILLET, D., COTTA, R., 2011, Thermal Measurements and Inverse Techniques, CRC Press, Boca Raton.

14 KAIPIO, J.P., SOMERSALO, E., 2004, "Computational and Statistical Methods for Inverse Problems", Springer, Berlin.

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