APPLICATION OF THE MARKOV CHAIN MONTE CARLO METHOD TO ESTIMATION OF PARAMETERS IN A MODEL OF ADSORPTION-ENHANCED REACTION PROCESS FOR MERCURY REMOVAL FROM NATURAL GAS

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ABSTRACT – A mathematical model proposed in the literature for the adsorption of mercury was solved numerically. This model involved the diffusion in the adsorbent particle, followed by a chemical reaction inside the solid matrix. The model was obtained based on the differential mass balance for the solute in a volume element bed with an equation involving diffusion and a first-order chemical reaction. For the direct solution of the problem, the Method of Lines (MOL) was applied to simplify the system of Partial Differential Equations (PDEs) into a system of time dependent Ordinary Differential Equations (ODEs). For the estimation of parameters, simulated measurements were generated with a normal distribution, with the direct solution as the mean and deviations of 10% regarding the maximum value of the exact solution. The sensor is located at the exit of the bed. Lastly, based on the sensitivity analysis, two parameters were chosen and estimated by the Markov Chain Monte Carlo (MCMC) method regarding the Gaussian distribution as a prior distribution to unknown parameters. In the estimation, the mean equal to the reference value with a standard deviation of 10% of the reference values. The results showed that the method was able to reproduce the reference values with relative errors of less than 3% for both the parameters.

1. INTRODUCTION

Mercury can be released either from natural and anthropogenic sources. Anthropogenic sources of mercury are commonly the combustion of fossil fuels associated with energy or heat production in power plants and waste incineration plants. These contribute for approximately 70% of total emissions into the atmosphere (Unep, 2008). Furthermore, mercury is subject to many studies due to its adverse effects on human health, high toxicity and bio-accumulative properties (Camargo et al., 2014).

The reference work provides a process model that comprises the superficial adsorption of mercury, the diffusion in the adsorbent particle and the chemical reaction in the solid matrix. The chemical reaction mechanism is included in the model in order to explain the high capacity for mercury fixation of the adsorbents that were used, previously confirmed by leaching stabilization results and heat treatment tests. In the simulations was observed the influence of mercury fixation.
on the dynamic behavior of the fixed bed column. The model proposed by Camargo et al. (2014) describing the removal of mercury from gaseous streams using modified hydroxyapatites is given by the following equations:

\[
\begin{align*}
\frac{\partial C_f}{\partial t} + u_0 \frac{\partial C_f}{\partial z} + (1-\varepsilon) \frac{\partial q}{\partial t} + (1-\varepsilon) \frac{\partial q_{RO}}{\partial t} &= 0; \quad t > 0; \quad 0 < z < L \\
\frac{\partial q}{\partial t} &= \frac{15D_{df}}{R_p^2} (q_{Rp} - \bar{q}) - \frac{\partial q_{RO}}{\partial t}; \quad t > 0; \quad 0 < z < L \\
\frac{\partial q_{RO}}{\partial t} &= k (q_{ROm} - q_{RO}) \bar{q}; \quad t > 0; \quad 0 < z < L \\
C_f &= 0; \quad \bar{q} = 0; \quad q_{RO} = 0 \quad \text{at} \quad t = 0 \\
C_f &= C_{f0} \quad \text{at} \quad z = 0; \quad \text{where} \quad q_{Rp} = HC_f \quad \text{(Henry's Law)}
\end{align*}
\]

The parameter \( \kappa \) was calculated by the expression \( \kappa = H (1-\varepsilon)/\alpha \varepsilon \) and the arbitrary parameter \( \alpha = 10^6 \) was chosen to maintain the magnitude of the non-dimensional variables near unit (Camargo et al., 2014).

2. MARKOV CHAIN MONTE CARLO (MCMC) METHODS

Advancements in computational methods allowed for Bayesian inference to expand its applicability. Among other methods, Markov Chain Monte Carlo stands out and is known simply as MCMC. There are several algorithms used for the definition of Markov Chains and that are suitable for Bayesian inference such as Metropolis, Metropolis-Hasting, Gibbs-Sampler, and hybrids. The most common MCMC technique is the Metropolis-Hastings algorithm (Gamerman, 1997, Orlande et al., 2011), which is the technique presented in this work. The implementation of the Metropolis-Hastings algorithm starts with the selection of a proposal distribution \( p(P^*, P^{(t-1)}) \), which is used to draw a new candidate state \( P^* \), given the current state \( P^{(t-1)} \) 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 \( P^* \) from the proposal distribution \( p(P^*, P^{(t-1)}) \).
2. Calculate the acceptance factor:

\[
AF = \min \left[ 1, \frac{\pi(P^*|Y)p(P^{(t-1)}|P^*)}{\pi(P^{(t-1)}|Y)p(P^*|P^{(t-1)})} \right]
\]

3. Generate a random value \( U \), which is uniformly distributed on \((0, 1)\).
4. If \( U \leq AF \), set \( P^{(t)} = P^* \). Otherwise, set \( P^{(t)} = P^{(t-1)} \).
5. Return to step 1 while some convergence criteria is not satisfied.

Therefore, a sequence is generated to represent the posterior distribution. Inferring on this distribution is obtained from inference on the samples \( \{P^{(1)}, P^{(2)}, ..., P^{(n)}\} \). However, we note that values of \( P^{(i)} \) must be ignored while the chain has not yet converged to equilibrium (the warm-up
period). In this work, the proposal was chosen as a random walk in the form:

\[ P^* = P^{(t-1)} + \omega P^{(t-1)} \varepsilon \]  

where \( \varepsilon \) is a random vector with a standard normal distribution, i.e., \( \varepsilon \sim N(0,1) \).

3. RESULTS

To select the parameters to be estimated, a sensitivity analysis was performed, evaluating the magnitude and the linear dependence between the parameters. From this analysis, there was noticed a linear dependence between \( \sigma \) and \( \kappa \). Since these parameters show high and close magnitudes, any choice would be acceptable. It was also observed a linear dependence between \( R_p \) and \( D_{if} \), and the parameter \( R_p \) showing a higher magnitude. Nonetheless, as the radius of the particle can be determined effortlessly, by means of a particle size analysis, the parameters chosen for the estimation were \( \kappa \) and \( D_{if} \).

Table 1 displays the results of the estimates (mean ± standard deviation) of the parameters \( \kappa \) e \( D_{if} \). A 10% deviation of simulated measurements and a deviation of parameters for the Gaussian distribution were also used. For the mean and standard deviation calculations of the estimates, the warm-up period, defined as the number of states required for the estimated value to begin to oscillate around a mean, was neglected. In both two analyzed scenarios, 5000 states were used in the Markov Chain. Figures 1 and 2 exhibit the breakthrough curves for Cases 1 and 2 for the dimensionless concentration and in Figures 4 to 6 the evolution of the Markov Chains for the two parameters estimated in each analyzed case.

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
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<tbody>
<tr>
<td></td>
<td>Mean (( \mu )) ± standard deviation (( \sigma ))</td>
<td>Exact (Camargo et al., 2014)</td>
</tr>
<tr>
<td>( \kappa ) (-)</td>
<td>1.9674±0.0050</td>
<td>1.9474</td>
</tr>
<tr>
<td>( D_{if} ) (m(^2)/s)</td>
<td>4.1508x10(^{-14}) ± 3.7701x10(^{-15})</td>
<td>4.1929x10(^{-14})</td>
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Figures 1 and 2 – Breakthrough curves for Cases 1 and 2.
4. CONCLUSIONS

Only simulated measurements were utilized in this work, aiming to evaluate the application of the proposed methodology. However, new studies must be conducted using experimental data for a new estimative of the parameters. The results obtained by the Markov Chain Monte Carlo method, using the Metropolis-Hastings algorithm, are very satisfactory for the parameters estimation in the proposed mercury adsorption model. The Markov Chains reached equilibrium at roughly 300 iterations and the parameters obtained have relative errors of less than 3% related to the reference.

5. REFERENCES