Use of Bayesian Methods in the Process of Uranium Bioleaching by *Acidithiobacillus ferrooxidans*

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Abstract: This research is focused on investigating the utilization of Bayesian methodologies, specifically the Markov Chain Monte Carlo method, as well as filter sampling by importance and sequential resampling. The objective is to estimate kinetic parameters and state variables associated with the uranium bioleaching process by *Acidithiobacillus ferrooxidans*. Experimental data of cell concentration, uranium concentration, and concentrations of ferrous and ferric ions, obtained from literature, were employed. These measurements were evaluated using a mathematical model expressed by a system of ordinary differential equations. Three different mathematical models were evaluated, considering different uncertainties in experimental measurements and mathematical models (1% and 5%). The estimation results presented a good fit to the experimental data, with coefficients of determination in the range of 0.95 to 0.99. The validation of the mathematical models was obtained by reproducing the experimental measurements and the Bayesian techniques proved to be suitable for application in the bioleaching process.

Keywords: Markov Chain Monte Carlo method; SIR particle filter; *Acidithiobacillus ferrooxidans*

1. Introduction

The increase in world demand for mineral goods, combined with the progressive depletion of reserves containing high levels of metals of economic interest and the need to guarantee nuclear fuel for the continuous operation of nuclear power plants in energy production, makes it important to develop alternatives for the treatment of ores containing low levels of these metals, such as uranium [1]. Bioleaching is a green technology for extracting, concentrating, or recovering metals from ores or waste, being an environmentally sustainable alternative to conventional hydrometallurgical processes [2–4].

The recovery of low-grade minerals has become one of the major concerns in mineral exploration. In this context, bacterial leaching, or bioleaching, arises, a technique based on the metabolic activity of microorganisms, which catalyze the process involving the oxidation of iron and the reduction of inorganic sulfur compounds, producing sulfuric acid and ferric ion [5].

Biodyrometallurgy has experienced significant advancement, with the utilization of microorganisms in ore treatment emerging as the most rapidly evolving domain in this field [6]. Several bacteria have already been cataloged and studied in the bioleaching process. Among the most common genera of prokaryotes found in acid-draining heap leach sites is the bacterial species *Acidithiobacillus ferrooxidans* [7].
Acidithiobacillus ferrooxidans is classified as a chemolithotrophic bacterium, meaning it derives its energy from the oxidation of inorganic substrates, basically ferrous ion, and reduced sulfur compounds, including metallic sulfides. Furthermore, it operates as an autotrophic organism, necessitating a supply of nitrogen, phosphorus, and magnesium, in addition to an inorganic source of energy [8]. With the discovery of this bacterium, studies on new extraction techniques and other bacterial species that could play important direct or indirect roles in this metal extraction and recovery process have been intensified [9].

The process of uranium bioleaching and the development of Acidithiobacillus ferrooxidans are influenced by various factors. One crucial parameter is the pH of the nutrient medium, playing a pivotal role in shaping the bioleaching process. As pH increases, proton availability decreases, leading to a slowdown in the oxidation reaction. At elevated pH levels, an excessive product layer forms on ore particle surfaces, creating a barrier between ore particles and metabolites. Research indicates that the optimal pH range for the growth of Acidithiobacillus ferrooxidans falls between 1.5 and 2.5. Temperature is also a significant factor in bioleaching; higher temperatures enhance the leaching rate, although excessively high temperatures can impede microbial growth and activity. Optimal temperatures for this process typically hover around 30 °C [10,11].

Increasing the pulp density can enhance ore loading and leach plant utilization rates. However, once the concentration limit is exceeded, it leads to the accumulation of specific metal ions in the solution, exceeding the tolerance limit of microorganisms and thereby inhibiting microbial growth and activity. Hence, slurry concentration ranges between 5% and 10% are considered acceptable [10–12].

Considering results presented by Romero-González et al. [13] regarding the ex situ bioremediation of mine water contaminated with U(VI) using Acidithiobacillus ferrooxidans strains, it was observed that elevated uranium concentrations can be detrimental to Acidithiobacillus ferrooxidans. This toxicity has the potential to result in a reduction in the efficiency of the bioleaching process.

Studying the kinetics of bioleaching kinetics holds importance in assessing the rate at which metals are solubilized by bacteria. An important approach to evaluating reaction kinetics is to use mathematical modeling to understand the mechanisms of the bioleaching process [14]. The formulation of mathematical models to represent bioleaching kinetics becomes a challenge since it is not possible to directly measure the parameters and because the models generally presented high levels of uncertainty. In this work, two Bayesian techniques were used: Markov Chain Monte Carlo method (MCMC) and the Sampling Importance Resampling (SIR) particle filter.

The objective of applying two techniques is, initially, to apply the MCMC for parameter estimation without considering the model’s uncertainty, since in this first stage, the uncertainties are associated only with the parameters. After this step, the particle filter methodology is used to enter the uncertainties associated with the model.

In this work, the validations of the applied techniques were carried out considering experimental data present in the literature of cell, uranium, ferrous, and ferric ion concentrations, using different case studies, which involved associated uncertainties of 1 and 5% both for the observable variables (experiment) regarding the models (1 and 5%).

2. Direct Model

Considering the phenomenon based on the bioleaching mechanism, a mathematical model was established to describe the bioleaching process of uranium by Acidithiobacillus ferrooxidans, where a phenomenon can occur directly in which the microorganism attacks the metal, or indirectly, when the byproduct of the metabolism of the microorganism oxidizes the metal, solubilizing it [15,16]. However, for the present model, the indirect bioleaching mechanism was considered to evaluate the phenomenon in which microorganisms do not maintain direct contact with the mineral during the process; that is, the agents are created by microbes that will oxidize the ore, as illustrated in Figure 1 [17–19].
In Equation (1), the metabolic reaction for bioleaching in the indirect mechanism is presented, which represents the global stoichiometry for Fe(II) oxidation [20].

$$\text{Fe}^{2+} + 0.2223\text{O}_2(g) + 0.0278\text{CO}_2(g) + 0.0056\text{NH}_4^+ + 0.9944\text{H}^+ \rightarrow \text{Fe}^{3+} + 0.0056\text{C}_2\text{H}_2\text{O}_2\text{N} + 0.4889\text{H}_2\text{O}$$  \(\text{(1)}\)

According to Vilcaez and Inoue [21], when bacteria derive energy exclusively from the oxidation of [Fe^{2+}] and allocate all energy towards bacterial growth, inhibitory processes affect the rate of cell growth. According to Madigan et al. [22], the inhibitory effect is denoted by blocking the cell multiplication of the microorganism by reversibly binding to the ribosomes, inhibiting protein synthesis, resulting in the slow death of the microbial population. When exposed to conditions favorable to bacterial growth, microorganisms reproduce again, and the population grows [16]. Equation (2) represents the cellular process without inhibitory effects.

$$r_{cell} = \frac{d[cell]}{dt} = \mu[cell] = \mu^{\text{max}} \frac{[\text{Fe}^{2+}]}{k_s + [\text{Fe}^{2+}]}$$  \(\text{(2)}\)

where [cell] is the biomass concentration, \(\mu\) is the specific coefficient of bacterial growth in iron oxidation, \(\mu^{\text{max}}\) is the maximum specific rate of bacterial growth, [Fe^{2+}] is the ferrous ion concentration, and \(k_s\) is the substrate saturation constant. For the present work, it was considered that the ferrous ion is the limiting substrate.

The inhibition process of Fe(II) oxidation affects cell growth, caused both by the [Fe(III)] reaction product, by a certain concentration of Fe(II), or even by the substrate itself [23,24]. The inhibitory influence of substrate [Fe^{2+}], product [Fe^{3+}], bacterial cells, and concentrations of heavy metals on the Fe(II) oxidation rate and bacterial growth are represented in Equation (3).

$$\mu = \mu^{\text{max}} \frac{[\text{Fe}^{2+}]}{k_s \left(1 + \frac{[\text{Fe}^{3+}]}{k_p}\right) + [\text{Fe}^{2+}]}$$  \(\text{(3)}\)

where [Fe^{3+}] is the ferric ion concentration, and \(k_p\) is the product inhibition constant. Assuming that substrate inhibition can be represented by Equation (4):

$$\mu = \frac{\mu^{\text{max}}[\text{Fe}^{2+}]}{k_s + [\text{Fe}^{2+}] + \frac{[\text{Fe}^{2+}]^2}{k_i}}$$  \(\text{(4)}\)

where \(k_s\) is the substrate inhibition constant.

According to Ojumu et al. [25], metal ions present different inhibitory processes, which affect microbial physiology. This inhibitory effect depends on the metallic concentration to which the microorganisms were exposed. If the concentration is not enough, they enter a phase of prolonged latency until their complete adaptation to the conditions is satisfactory.
In the construction of the mathematical model, the oxidation of uraninite by oxidants other than Fe\(^{3+}\) and the effect of contaminants on the leaching kinetics are assumed to be insignificant. The integration of immediate iron species concentrations accounts for the effect of Fe impurities. According to Rashid et al. [19] and Vilcaez and Inoue [21], uraninite leaching is caused by anodic oxidation by [Fe\(^{3+}\)]. As a result, the following kinetic equation for uranium bioleaching is considered:

\[
r_U = \frac{d[U]}{dt} = -k_1 \left( \frac{[Fe^{3+}]}{[Fe^{2+}]} \right)^n \left( \frac{[Fe^{3+}]}{k_2 \left( \frac{[Fe^{3+}]}{Fe^{2+}} \right)^n + [Fe^{2+}]} \right)^m \tag{5}
\]

where \(r_U\) is the rate of dissolution of uranium, \([U]\) is the concentration of uranium in the solid phase, and \(k_1, k_2, n, m\) are constants. The production and use of [Fe\(^{2+}\)] is expressed by Equation (6), where the formation rate is equivalent to the oxidation rate of uranite. This oxidation is enzymatically catalyzed by bacteria, establishing a direct proportionality to the growth rate of microorganisms [19].

\[
\frac{d[Fe^{2+}]}{dt} = 2 \frac{M_{Fe}}{M_U} (-r_U) - \frac{1}{Y_{cell/Fe^{2+}}} (r_{cell}) \tag{6}
\]

where \(M_{Fe}\) is the molecular mass of iron, \(M_U\) is the molecular mass of uranium, and \(Y_{cell/Fe^{2+}}\) is the ferrous ion conversion factor in cells. Equation (7) presents the ferric balance system, where [Fe\(^{3+}\)] is generated by bacteria and utilized in the oxidation of uranite, with the possibility of undergoing precipitation [19].

\[
\frac{d[Fe^{3+}]}{dt} = \frac{1}{Y_{cell/Fe^{2+}}} (r_{cell}) - 2 \frac{M_{Fe}}{M_U} (-r_U) - (-r_{Fe^{3+}\text{precipitated}}) \tag{7}
\]

From the variation in total iron concentrations, it can be inferred that precipitation occurs at the rate of Fe (III) rate, as indicated by Equation (8).

\[
r_{Fe^{3+\text{precipitated}}} = -k_3 \left( \frac{[Fe^{3+}]}{[Fe^{2+}]} \right)^q \left( k_4 + \frac{[Fe^{3+}]}{[Fe^{2+}]} \right)^p \tag{8}
\]

where \(k_3, k_4, q, p\) are constants.

The system of ordinary differential equations (ODEs) presented in Equations (2) and (5)–(7) constitutes the mathematical model for the uranium bioleaching process, as investigated by [19]. Furthermore, Equations (3) and (4) provide alternative formulations for representing the specific velocity of cell growth, which will be evaluated in the present work together with Equation (2).

3. Bayesian Techniques—MCMC and Particle Filter

The Markov Chain Monte Carlo method and the Sampling Importance Resampling particle filter, used to estimate parameters and state variables, were applied using Matlab\textsuperscript{®} software, version R2022b. In this study, three distinct models were used, each incorporating a different formulation for the specific speed of cell growth in each one of them. In Equations (2)–(4), each replacement represents a different ODE system to be evaluated; for model 1, Equations (2), (5)–(7), for model 2, Equations (3), (5)–(7), and for model 3, Equations (4)–(7).
Based on the evaluated models, three different parameter vectors were used for each model: \( P_1 \), \( P_2 \), and \( P_3 \), represented in Equations (9)–(11) for models 1, 2, and 3, respectively. The vector of status variables was represented as \( Y^{VE} \), according to Equation (12).

\[
P_1 = [k_1, k_2, k_3, k_4, k_5, n, m, q, p, Y_{cell}, \mu_{max}]
\]

\[
P_2 = [k_1, k_2, k_3, k_4, k_5, n, m, q, p, Y_{cell}, \mu_{max}, k_p]
\]

\[
P_3 = [k_1, k_2, k_3, k_4, k_5, n, m, q, p, Y_{cell}, \mu_{max}, k_s]
\]

\[
Y^{VE} = [U_{cell}, Fe^{2+}, Fe^{3+}]
\]

In the Bayesian approach, information about the parameters that appear in the problem formulation, available before measurements and coded according to a probability distribution, can be considered, along with information from experimental measurements, to improve the statistical inference process. Therefore, solving the inverse problem by the Bayesian method means obtaining the posterior probability density [26].

The information obtained by the experimental measurements is combined with that assumed for the parameters before carrying out the measurements through the mechanism known as Bayes’ theorem [27–29]:

\[
\pi_{posterior}(P) = \pi(P|\text{exp}) = \frac{\pi_{prior}(P)\pi(\text{exp}|P)}{\pi(\text{exp})}
\]

where \( \pi_{posterior}(P) \) is the posterior probability distribution, \( \pi_{prior}(P) \) is the prior probability distribution, \( \pi(\text{exp}|P) \) is the likelihood function, and \( \pi(\text{exp}) \) is the marginal probability distribution of the measurements, which represents a normalization constant.

There are situations in which the corresponding probability distributions presented in Equation (13) cannot be obtained analytically. In these cases, there is a need to use simulation techniques that use samples of \( \pi(P|\text{exp}) \) to obtain information about \( P \). Among these techniques, the Markov Chain Monte Carlo method stands out when a posteriori calculation involves parameter estimates, and the Particle Filter when estimates of status variables are obtained.

### 3.1. Markov Chain Monte Carlo Method

The Markov Chain Monte Carlo method is used to generate samples from the posterior distribution and obtain sample estimates for the characteristics of this distribution using iterative simulation techniques. One of the widely utilized algorithms for implementing the Markov Chain Monte Carlo method is the Metropolis–Hastings algorithm, which was utilized in the present study [30,31].

The construction of the Markov Chain involves a sequence of random variables, \( \{P^{(1)}, P^{(2)}, \ldots, P^{(n)}\} \) where the next state, \( P^{(i+1)} \), is derived from a distribution \( q(P^{(i+1)}|P^{(i)}) \) which only depends on the current state \( P^{(i)} \) but not explicitly on previous states. This sequential process is called a Markov Chain, and the distribution \( q(P^{(i+1)}|P^{(i)}) \) is referred to as the transition kernel or transition density of the chain. In this work, a proposed distribution \( q(P^*, P^{(i−1)}) \) was used to generate a new candidate parameter vector \( P^* \), dependent only on the current state but not explicitly on the previous states, \( P^{(i−1)} \). This new parameter vector \( P^* = P^{(i−1)}(1 + \omega\epsilon) \) was randomly generated using a Gaussian transition kernel, characterized by a mean \( P^{(i−1)} \) and standard deviation \( \omega P^{(i−1)} \), where \( \epsilon \) is a random variable drawn from a Gaussian probability distribution with a mean of zero and standard deviation equal to 1, denoted as 1, N (0,1) [27,30–41].

### 3.2. Particle Filter—SIR

The SIR particle filter depends on both the state evolution model and the measurement model, being used as a tool for estimating state variables. Filter initialization consists
of generating samples from a given set of the probability distribution that represents the uncertainty associated with the initial condition with the number of \( N_{\text{part}} \), samples, such that this information is equivalent to the number of particles. The particles can be represented vectorially by Equation (14) [42–44]:

\[
X_k^i = \begin{bmatrix}
  x_1 \\
  x_2 \\
  \vdots \\
  x_Q
\end{bmatrix}_k^i
\text{ for } \{ i = 1, \ldots, N_{\text{part}}; k = t_0, t_1, \ldots, t_{\text{fim}} \}
\]

(14)

where \( Q \) is the total number of nodes in the mesh. Thus, the SIR filter algorithm is started by generating some particles, \( N_{\text{part}} \), so that, Equation (15):

\[
X_k^i \quad \{ i = 1, \ldots, N_{\text{part}}; k = t_0 \}
\]

(15)

It should be noted that vector \( X \) represents the state variables, which are cell, uranium, \( \text{Fe}^{2+} \), and \( \text{Fe}^{3+} \) concentrations. Then, the weights related to each particle are calculated, as shown in Equation (16):

\[
W_k^i \quad \{ i = 1, \ldots, N_{\text{part}}; k = t_0, t_1, \ldots, t_{\text{fim}} \}
\]

(16)

The algorithm for the SIR particle filter is presented below [42–44]:

1. Start
   1.1 Take a set of particles of initial distributional \( \pi(X_0) \) and obtain \{ \( X_0^i, W_0^i \); \( i = 1, \ldots, N_{\text{part}} \) \}
   1.2 Do \( k = 1 \)
2. Evaluation of the weights: advance the states in time \( k - 1 \) for time \( k \) using the state evolution model \( X_k = f_k(X_{k-1}, v_k) \), where \( f \) is in general a non-linear function that depends on \( X \) and has uncertainties represented by \( v \).
   2.1 Calculate the new weights \( W_k^i \)
   2.2 Normalize the weights \( \hat{W}_k^i = \frac{W_k^i}{\sum_{i=1}^{N_{\text{part}}} W_k^i} \)
3. Resampling
   3.1 Construct the sum of the cumulative weights, being computed by \( c_i = c_{i-1} + w_k^i \) for \( i = 2, \ldots, N_{\text{part}} \) with \( c_1 = 0 \)
   3.2 Take \( i = 1 \) and generate \( u_1 \) from a uniform distribution \( U[0, N^{-1}] \)
   3.3 For \( j = 1, \ldots, N_{\text{part}} \) do
      \( u_j = u_1 + N^{-1}(j - 1) \)
      While \( u_j > c_i \) do \( i = i + 1 \)
      Designate the particles \( X_k^j = X_k^i \)
      Assign the weights to \( W_k^j = N^{-1} \)
4. Calculation of the current state estimate
   \[ \pi(X_k|Z_k) \approx \sum_{i=1}^{N_{\text{part}}} X_k^i W_k^i \]
5. Do \( k = k + 1 \), if \( k = t_{\text{end}} + 1 \), then stop.
6. With the new particles, return to step two.
4. Results

In the present work, from the initial parameter estimates, the Markov Chain Monte Carlo method was used to estimate the parameters of the three evaluated models, with the uncertainties associated only with the parameters, without considering the uncertainties of the models. After estimating the parameters, the SIR particle filter was applied, considering the parameters estimated in the previous step and inserting the uncertainties associated with the models to validate the codes and, thus, analyze whether these models can predict the experimental measurements.

A uniform a priori probability distribution was assumed for the parameters, where initial estimates for the parameters were obtained from a priori information from the literature \[19\], used here as reference values \(P_{\text{ref}}\), and these were multiplied by a factor of 1.1. The initial estimates for the parameters are presented in Table 1.

Table 1. Reference values for initial estimates for kinetic parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(P_{\text{ref}}) [19]</th>
<th>Initial Estimate (1.1 (P_{\text{ref}}))</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>94.83</td>
<td>104.31</td>
<td>g/m³h</td>
</tr>
<tr>
<td>(k_2)</td>
<td>(6.01 \times 10^3)</td>
<td>(6.61 \times 10^3)</td>
<td>g/m³³</td>
</tr>
<tr>
<td>(k_3)</td>
<td>0.0034</td>
<td>0.0037</td>
<td>g³P/(m³)⁻¹h⁻¹</td>
</tr>
<tr>
<td>(k_4)</td>
<td>0.3651</td>
<td>0.4016</td>
<td>g/m³³</td>
</tr>
<tr>
<td>(k_s)</td>
<td>(2.49 \times 10^3)</td>
<td>(2.74 \times 10^3)</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>(n)</td>
<td>0.3845</td>
<td>0.4230</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>(m)</td>
<td>2.86</td>
<td>3.15</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>(q)</td>
<td>1.40</td>
<td>1.54</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>(p)</td>
<td>-0.3262</td>
<td>-0.3588</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>(Y_{\text{cell}/Fe^{2+}})</td>
<td>(2.25 \times 10^5)</td>
<td>(2.48 \times 10^5)</td>
<td>cell/(gFe^{2+})</td>
</tr>
<tr>
<td>(\mu_{\text{max}})</td>
<td>0.0864</td>
<td>0.095</td>
<td>h⁻¹</td>
</tr>
<tr>
<td>(k_p)</td>
<td>(2.5 \times 10^5)</td>
<td>(2.75 \times 10^5)</td>
<td>g/L⁻¹</td>
</tr>
<tr>
<td>(k_{si})</td>
<td>(2.5 \times 10^5)</td>
<td>(2.75 \times 10^5)</td>
<td>g/L</td>
</tr>
</tbody>
</table>

Table 2 presents the initial conditions of the state variables, which are the cell, uranium, Fe²⁺, and Fe³⁺ concentrations, which were obtained from the work of Rashidi et al. [19].

Table 2. Initial conditions.

<table>
<thead>
<tr>
<th>Cell (Cells/m³)</th>
<th>Uranium (g/m³)</th>
<th>Fe²⁺ (g/m³)</th>
<th>Fe³⁺ (g/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \times 10^{12})</td>
<td>(3.47 \times 10^3)</td>
<td>(3.85 \times 10^3)</td>
<td>500</td>
</tr>
</tbody>
</table>

For each model, a Gaussian uncertainty was considered with means equal to the value of the state variable, \(Y_{\text{VE}}\), and standard deviation being the model error. A study of the variation of measurement deviations and model error was carried out, and the measurement deviation was calculated in relation to the maximum value of the respective state variable, as shown in Table 3. The case study was carried out to verify which parameter presented the best estimate, with convergence to the posterior probability distribution and, consequently, more accurate parameter values. For each case study, all parameters of the referred models were submitted to the estimation process.

Table 3. Measurement deviation and model error.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Measurement Deviation</th>
<th>Model Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1% max (Y_{\text{VE}})</td>
<td>5%</td>
</tr>
<tr>
<td>2</td>
<td>5% max (Y_{\text{VE}})</td>
<td>1%</td>
</tr>
<tr>
<td>3</td>
<td>1% max (Y_{\text{VE}})</td>
<td>1%</td>
</tr>
<tr>
<td>4</td>
<td>5% max (Y_{\text{VE}})</td>
<td>5%</td>
</tr>
</tbody>
</table>

For the Markov Chain Monte Carlo method, the number of Markov Chain states, \(N\), was defined as \(1 \times 10^4\). The search step used, \(\omega\), was \(1 \times 10^{-3}\). For the particle filter, the
number of particles, \( N_{\text{part}} \), equal to 500 was defined. In both techniques, the experimental measurements were obtained by Rashidi et al. [19].

4.1. Estimates of Parameters Obtained by the Markov Chain Monte Carlo Method

For the analysis of the results in this study, it is recommended that the initial states of the chain are discarded as if they formed a heating sample. With increasing iterations, the chain tends to converge towards the distribution of interest, which is the posterior probability distribution of the parameters. Parameter estimates’ results were obtained considering a 99% credible interval (CI). To exemplify the convergence of the MCMC, Figure 2 corresponds to the states of the Markov Chains for the parameter \( q \) estimated in models 1, 2, and 3, respectively.

![Figure 2. Evolution of Markov Chains for the constant q, case 2, (a) model 1, (b) model 2, and (c) model 3.](image)

After the Markov Chain heating states, the posterior probability distribution was obtained, the result of which can be seen in Table 4 in terms of means and 99% credible intervals. Although the adjusted parameters are restricted to this study, the model equation is general and can be used in other bioleaching procedures. For example, Acidithiobacillus ferrooxidans is widely used in the bioleaching of a variety of metals from ores, including copper, nickel, cobalt, gold, and rare earth elements, in addition to uranium [45,46].

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>( k_1 )</td>
<td>108.86 (106.82; 111.34) g/m³h</td>
</tr>
<tr>
<td>Model 2</td>
<td>( k_2 (10^3) )</td>
<td>6.51 (6.43; 6.58) g/m³</td>
</tr>
<tr>
<td>Model 3</td>
<td>( n )</td>
<td>0.382 (0.380; 0.388) Dimensionless</td>
</tr>
<tr>
<td>Model 1</td>
<td>( k_3 )</td>
<td>0.009 (0.004; 0.004) Dimensionless</td>
</tr>
<tr>
<td>Model 2</td>
<td>( k_4 (10^3) )</td>
<td>3.00 (2.96; 3.06) Dimensionless</td>
</tr>
<tr>
<td>Model 3</td>
<td>( p \times (-1) )</td>
<td>0.402 (0.398; 0.405) Dimensionless</td>
</tr>
<tr>
<td>Model 1</td>
<td>( Y_{\text{cell/Fe}^{2+}} (10^9) )</td>
<td>2.28 (2.25; 2.31) Dimensionless</td>
</tr>
<tr>
<td>Model 2</td>
<td>( p_{\text{max}} )</td>
<td>0.097 (0.096; 0.098) Dimensionless</td>
</tr>
<tr>
<td>Model 3</td>
<td>( k_p (10^5) )</td>
<td>- Dimensionless</td>
</tr>
<tr>
<td>Model 1</td>
<td>( k_c (10^5) )</td>
<td>2.73 (2.72; 2.75) g/L−1</td>
</tr>
<tr>
<td>Model 2</td>
<td>( k_c (10^5) )</td>
<td>- Dimensionless</td>
</tr>
<tr>
<td>Model 3</td>
<td>( k_c (10^5) )</td>
<td>2.75 (2.71; 2.79) g/L−1</td>
</tr>
</tbody>
</table>

Table 4. Results of parameter estimates in terms of mean and 99% credible intervals.
4.2. Estimates of State Variables with the SIR Particle Filter

The results of the estimates of the state variables were obtained by the particle filter of Importance Sampling and Sequential Resampling. When applying this filter, the parameters were considered deterministically with the values in the means of the posterior probability distributions obtained in the first stage with the MCMC (see Table 4).

Figure 3 presents just some of the results of the estimates of the concentrations of the state variables [U], [cell], [Fe\(^{2+}\)], [Fe\(^{3+}\)], in terms of the mean and 99% credible interval, in comparison with the experimental measures obtained by Rashidi et al. [19].

![Comparison of estimated state variables with experimental measurements](image)

**Figure 3.** Comparison of estimated state variables with experimental measurements [19]: (a) case 1 of model 1; (b) case 2 of model 2; (c) case 3 of model 3; and (d) case 4 of model 3.

By calculating the coefficients of determination, it was possible to compare the estimated variables and experimental measurements. Table 5 presents the results for the determination coefficient for case 3 referring to models 1, 2, and 3.

<table>
<thead>
<tr>
<th>State Variables</th>
<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cell]</td>
<td>0.9617</td>
<td>0.9630</td>
<td>0.9559</td>
</tr>
<tr>
<td>[U]</td>
<td>0.9978</td>
<td>0.9963</td>
<td>0.9941</td>
</tr>
<tr>
<td>[Fe(^{2+})]</td>
<td>0.9904</td>
<td>0.9925</td>
<td>0.9934</td>
</tr>
<tr>
<td>[Fe(^{3+})]</td>
<td>0.9629</td>
<td>0.9574</td>
<td>0.9624</td>
</tr>
</tbody>
</table>

5. Discussion

It is verified in Figure 2 that the Markov Chains showed a tendency to converge to the equilibrium distribution for the constant \( q \) of the different evaluated models. For this parameter, less than 200 states were needed for the Markov Chain to converge to the value of approximately 1.402. It is observed in Table 4 that models 1, 2, and 3 presented values very close to each other. However, it is noted that for model 3, most parameters presented results closer to the reference values, when compared to models 1 and 2.

When comparing the value of the reference yield coefficient, \( Y_{\text{cell/Fe}^{2+}} = 2.25 \times 10^9 \) cells/(gFe\(^{2+}\)), with the results obtained for models 1, 2, and 3, it is observed that they are in the range of \( 2.24 \times 10^9 \) to \( 2.34 \times 10^9 \) cells/(gFe\(^{2+}\)). Previous studies reported values of \( 2.5 \times 10^{10} \) cells/(gFe\(^{2+}\)) [47], \( 2.4 \times 10^{10} \) cells/(gFe\(^{2+}\)) [48], \( 2.23 \times 10^{10} \) cells/(gFe\(^{2+}\)) [49], \( 1.7 \times 10^{10} \) cells/(gFe\(^{2+}\)) [50], and \( 2.3 \times 10^{10} \) cells/(gFe\(^{2+}\)) [51]. \( Y_{\text{cell/Fe}^{2+}} \) represents the...
yield of cells produced per gram of Fe\(^{2+}\) oxidized, reflecting the efficiency of bacterial metabolism [52]. The estimated values for this parameter show that bacterial growth is favored by the higher availability of Fe\(^{2+}\) as an energy source, as expected. The values of the present work differ from those reported in the literature due to the different experimental conditions, although present the same order of magnitude of the values.

Comparing the maximum rate of specific bacterial growth, \(\mu_{\text{max}} = 0.086 \text{ h}^{-1}\), with the results obtained for the different models, it is observed that they are in the range of 0.093 to 0.098 \text{ h}^{-1}. The literature reports results in the same order of magnitude as 1.78 \text{ h}^{-1} [23,53], and 0.047 \text{ h}^{-1} [54]. \(\mu_{\text{max}}\) represents the speed at which the cells divide, directly affecting the kinetics of the bioleaching process [55]. The estimated values for this parameter show that bacterial growth is limited by the low concentration of Fe\(^{3+}\), as reported in Vera et al. [56].

Similarly, it was also verified for the substrate saturation constant, \(K_s = 2.49 \times 10^3 \text{ g/m}^3\), where results for models 1, 2, and 3 are in the range of 2.79 \times 10^3 to 3.06 \times 10^3 \text{ g/m}^3, which have the same order of magnitude as the values presented in the literature, which are 0.3 \times 10^3 \text{ g/m}^3 [57]. In general, it was observed that the results obtained from the parameter estimates for models 1, 2, and 3, presented the same order of magnitude as the values found in the literature, with some differences due to the experimental conditions. This parameter represents the concentration of Fe\(^{2+}\) at which the bacterial growth rate is half of the maximum rate, indicating the sensitivity of the bacteria to the substrate [58]. The estimated values for this parameter show that the bacteria are able to grow at low concentrations of Fe\(^{3+}\), which is an advantage for the bioleaching process, as it reduces the need for nutrient addition [59].

Figure 3a shows the comparison of the uranium concentration estimates, in terms of the mean and 99% credible interval, with the experimental measurements, of case 1 of model 1. It was observed that there was a reduction in the uranium concentration during the bioleaching process and, after approximately 60 h, it showed stability. Due to bacterial oxidation of the mineral, there was an increase in the rate of bacterial growth and, consequently, the concentration of the mineral increased, which resulted in greater recovery by the bacteria until equilibrium was reached. This dynamic may be related to the generation of ferric ions in the process through bacterial oxidation of Fe\(^{3+}\), which increased bacterial growth and, consequently, the concentration of Fe\(^{3+}\), resulting in increased recovery of the metal by the bacteria until reaching stability [60].

Figure 3b shows the comparison of the Fe\(^{2+}\) concentration estimates, in terms of the mean and 99% credible interval, with the experimental measurements, referring to case 2 of model 2. A good agreement between the results is observed, meaning a well-adjusted result, since the Fe\(^{2+}\) concentration estimates agree with the experimental measurements. In this sense, the kinetic parameters that were adjusted for model 2 were also sufficient for reproducing the experimental concentration profiles. After 60 h of the experiment, the Fe\(^{2+}\) concentration tended to zero, indicating that the oxidation process of ferrous ions was practically complete. According to Li et al. [60], this decline in Fe\(^{3+}\) concentration may be related to the increase of ferric ions in the presence of microorganisms; that is, a precipitation process occurs when Fe\(^{2+}\) oxidizes to Fe\(^{3+}\). This implies that bacteria play a key role in the oxidation of ferrous ions in the solution, facilitating the uranium bioleaching process. According to Nie et al. [61], the consumption of Fe\(^{2+}\) is directly related to the growth of \(A. \text{ferrooxidans}\), even though it is inversely proportional to it.

Figure 3c shows the comparison of the Fe\(^{3+}\) concentration estimates, in terms of the mean and 99% credible interval, with the experimental measurements, of case 3 of model 3. It was verified that the results presented a good agreement between the estimates and experimental measurements. Thus, model 3 is also capable of reproducing the experimental concentration profiles used in the present work. Initially, in the first 40 h, an increase in the concentration of Fe\(^{3+}\) is observed, resulting in a greater recovery of the metal, followed by a decrease in the concentration. According to Li et al. [60], for optimized bioleaching, low initial values of Fe\(^{3+}\) are required. This behavior may be associated with the presence of ferric ions in the process or may be attributed to the mechanism used for metal recovery.
Figure 3d shows the comparison of the cell concentration estimates, in terms of the mean and 99% credible interval, with the experimental measurements, of case 4 of model 3, showing a good fit between estimated variables and experimental measurements. It was observed that the cells reached stability after approximately 50 h of the experiment. This stabilization could be associated with the reduced formation of ferric ions. Thus, as the reaction progressed, there was an increase in the bacterial population, as also reported by Abhilash et al. [18].

For the case presented in Table 5, it was observed that for the three studied models, there was a good fit of the estimates with the experimental measures. Model 1, which does not present inhibitory effects, proved to be more efficient for estimating uranium and Fe$^{3+}$, concentrations, while models 2 and 3, which considered inhibition by product and substrate, respectively, proved to be more adequate for the estimation of cell and Fe$^{2+}$, respectively.

6. Conclusions

In this work, Bayesian techniques, Markov Chain Monte Carlo method, and the SIR particle filter were applied in a model of uranium bioleaching by *Acidithiobacillus ferrooxidans*. Different models were evaluated, varying the specific cell growth rate, considering the terms associated with substrate and product inhibitions. Experimental measures from the literature were used for the inverse analysis of the problem. The results of parameter and state variable estimates were reported in terms of the mean and 99% credible interval.

The mathematical model used in this study was validated by accurately reproducing the experimental data, showing values of the determination coefficients greater than 0.95. Model 1, which did not show inhibitory effects, proved to be more efficient for estimating uranium and Fe$^{3+}$ concentrations, while models 2 and 3, which considered inhibition by product and substrate, respectively, proved to be more suitable for the estimate of cell and Fe$^{2+}$ concentration, respectively.

Bayesian techniques have provided measures of uncertainty about parameter and state variable estimates, such as credible intervals, which are useful for assessing goodness of fit and comparing different models. These results are important to obtain more precise information about the process and the influence of different variables in the bioleaching process, contributing to making it more efficient and economical.

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Nomenclature

- **cell**: Biomass concentration (cell/m³)
- **µ**: Specific rate of bacterial growth (h⁻¹)
- **µmax**: Maximum specific rate of bacterial growth (h⁻¹)
- **[Fe²⁺]**: Ferrous ion concentration (g/m³)
- **k_s**: Substrate saturation constant (g/cm³)
- **[Fe³⁺]**: Ferric ion concentration (g/m³)
- **k_p**: Product inhibition constant (g/L⁻¹)
- **k_{si}**: Substrate inhibition constant (g/L)
- **Fe**: Iron
- **r_U**: Uranium dissolution rate
- **[U]**: Uranium concentration in the solid phase (g/m³)
- **k_1, k_2, n, m**: Constants (g/m³h) (g/m³)
- **M_{Fe}**: Molecular mass of iron (u)
- **M_{U}**: Molecular mass of uranium (u)
- **Y_{cell/Fe}²⁺**: Ferrous ion conversion factor in cells (cell/ (g Fe²⁺))
- **P**: Vector of estimated parameters
- **N**: Number of Markov Chain states
- **w**: Search Step
- **SIR**: Sampling by importance and sequential resampling
- **N_{part}**: Number of particles
- **t_{end}**: End time of experiment
- **Q**: Total number of mesh nodes
- **IC**: Credible interval
- **MC**: Markov Chain Monte Carlo method
- **U**: Uranium
- **K_3, K_4, η, p**: Constants (g⁻¹⁻³ /m³)⁻¹⁻³ h⁻¹
- **X**: State variables
- **Y_{VE}**: Vector of estimated state variables
- **P_1, P_2, P_3**: Parameters vector

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