

# Numerical Simulation of $\gamma$ -Valerolactone Adsorption into Porous Spheres in a Batch Process

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The production of ethanol from lignocellulosic biomass is more complex in relation to ethanol produced from feedstock containing sugars or starch, since it requires the conversion of polysaccharides, cellulose or hemicellulose, into fermentable sugars. An alternative to improve this conversion of biomass polysaccharides into sugars is the use of  $\gamma$ -valerolactone (GVL) as a solvent. However, the GVL must be removed before the fermentation, since its presence is harmful to the microorganisms that metabolize glucose to produce ethanol. One extraction technique is the use of subcritical CO<sub>2</sub>, which is able to separate large amounts of GVL, but a complementary method is still required to separate small quantities of GVL remaining in the sugar solution, which can be done efficiently with adsorption. In this work, the adsorption of  $\gamma$ -valerolactone by porous spheres made of a resin in batch mode is studied to remove the GVL from the sugar solution containing glucose. This work is computational and the modelling considers the mass transfer from the solution to the surface of the spheres, the diffusion inside the pores of the spheres, and then the adsorption of GVL. The numerical resolution is done using two numerical methods, the finite differences and the variational method. The results are compared using different numbers of radial intervals in the spherical particles.

**Keywords:** biomass, ethanol, glucose,  $\gamma$ -valerolactone, adsorption, finite differences, variational formulation.

## 1. Introduction

Ethanol can be produced from lignocellulosic biomass by the hydrolysis of cellulose and hemicellulose into monosaccharides (sugars). Lignocellulosic sources available at industrial scale are corn crop residues and sugarcane bagasse, for example, but there are many others. However, the hydrolysis process of these materials is complex and expensive, so improvements are required to make this process economically viable.

It has been shown that  $\gamma$ -valerolactone (GVL) as solvent in the conversion of the lignocellulosic biomass into sugars, in the presence of low concentration acid, has advantages over water alone (Mellmer et al., 2014), with increased catalytic activity (Alonso et al., 2013), and higher selectivity and efficiency of the hydrolysis reaction, minimizing sugar degradation (Luterbacher et al., 2014). After the hydrolysis, GVL must be separated from the sugar solution, because a high concentration of this solvent is harmful in the fermentation stage, due to its toxicity to the microorganisms that metabolize glucose to produce ethanol. It was found that an extraction with subcritical CO<sub>2</sub> was able to decrease the concentration of GVL, but a further separation was still required in order to reduce the GVL to acceptable levels (Luterbacher et al. 2014).

Adsorption has been found to have high efficiency as a complementary separation step to selectively remove GVL from the solution (Trindade, 2015a; Trindade et al, 2015b). Trindade (2015a) evaluated the use of four adsorbents in the removal of GVL from the glucose solution, and found that the resin Sepabeads SP850, which is a highly porous styrenic adsorbent, was the most selective to adsorb GVL compared to glucose.

The objective of this work was to model the adsorption of GVL into spheres of SP850 in a batch process, in order to reproduce the batch experimental results obtained by Trindade (2015a), and thus help improve this separation step. The model considers both external and internal mass transfer, using a Langmuir type isotherm for adsorption in the spheres, and was solved with two numerical methods, finite differences and variational method. The results were then compared with the experimental data available.

## 2. Mathematical Model

Adsorption in a porous medium is a very important separation process, for a variety of substances. For a batch system containing a volume of solution ( $V$ ) and a volume of porous spheres ( $v$ ), the modeling of the solute concentration in the solution,  $C(t)$ , and in the spheres,  $c(r, t)$ , can be written as a set of differential equations (Horstmann and Chase, 1989). In this work, a Langmuir type isotherm is considered, given as:

$$q = \frac{q_m \cdot b \cdot c}{(1 + b \cdot c)} \quad (1)$$

where  $q$  is the amount of solute adsorbed in the spheres, and  $q_m$  is the maximum amount of solute that can be adsorbed by the spheres. The model can then be made dimensionless by defining  $u = c/C_0$  and  $w = C/C_0$  (Guirardello, 2013), so that:

$$f'(u) \cdot \frac{\partial u}{\partial \tau} = \frac{1}{x^2} \cdot \frac{\partial}{\partial x} \left[ x^2 \cdot \frac{\partial u}{\partial x} \right] \quad (2)$$

$$\frac{dw}{d\tau} = -\alpha \cdot [w - u(1, \tau)] \quad (3)$$

with boundary and initial conditions given by:

$$\frac{\partial u}{\partial x} = \beta \cdot (w - u) \quad \text{at } x = 1 \quad \tau > 0 \quad (4)$$

$$\frac{\partial u}{\partial x} = 0 \quad \text{at } x = 0 \quad \tau > 0 \quad (5)$$

$$u = 0 \quad \text{at } \tau = 0 \quad 0 \leq x \leq 1 \quad (6)$$

$$w = 1 \quad \text{at } \tau = 0 \quad (7)$$

where  $x = r/R$ ,  $\tau = t \cdot D/R^2$ , and:

$$\alpha = 3 \cdot \frac{v}{V} \cdot \left( \frac{R \cdot k_f}{D} \right) \quad (8)$$

$$\beta = \left( \frac{R \cdot k_f}{\varepsilon \cdot D} \right) \quad (9)$$

$$f'(u) = 1 + \frac{(1 - \varepsilon)}{\varepsilon} \cdot \frac{q_m \cdot b}{(1 + b \cdot C_0 \cdot u)^2} \quad (10)$$

## 3. Methodology

Two numerical approaches were used in this work to make the discretization in the  $x$  variable: finite differences and variational calculus. Both approaches are detailed here.

### 3.1 Finite Differences

The finite differences method is well known and is based on the substitution of the exact derivatives by numerical ones. However, here it is used appropriate expressions for the boundary points ( $x = 0$  and  $x = 1$ ), so that the boundary conditions are naturally inserted in the numerical resolution of the PDE:

$$\left( \frac{\partial^2 u}{\partial x^2} \right) \Big|_i = u_i'' \cong \frac{-7 \cdot u_i + 8 \cdot u_{i+1} - u_{i+2} - 6 \cdot \Delta x \cdot u_i'}{2 \cdot \Delta x^2} \quad i = 0 \quad \text{or } x = 0 \quad (11)$$

$$\left( \frac{\partial^2 u}{\partial x^2} \right) \Big|_i = u_i'' \cong \frac{-7 \cdot u_i + 8 \cdot u_{i-1} - u_{i-2} + 6 \cdot \Delta x \cdot u_i'}{2 \cdot \Delta x^2} \quad i = N \quad \text{or } x = 1 \quad (12)$$

Both expressions are second order in the interval (error  $\sim \Delta x^2$ ) and make use of the known first derivative, so that the boundary conditions can be inserted directly. There is no need for similar expressions for the first derivatives, since they are given by the boundary conditions at these two points:

$$\left(\frac{\partial u}{\partial x}\right)\Big|_i = u'_i = 0 \quad i = 0 \text{ or } x = 0 \quad (13)$$

$$\left(\frac{\partial u}{\partial x}\right)\Big|_i = u'_i = \beta \cdot (w - u_i) \quad i = N \text{ or } x = 1 \quad (14)$$

However, at  $x = 0$  the L'Hospital theorem must be applied in Eq (2) in order to avoid getting  $0/0$ , since the first derivative is divided by  $x$  after rearrangement of the right hand side of that equation.

For the interior points ( $x_i, i = 1, \dots, N - 1$ ), the usual second order expressions (error  $\sim \Delta x^2$ ) are used:

$$\left(\frac{\partial^2 u}{\partial x^2}\right)\Big|_i = u''_i \cong \frac{u_{i+1} - 2 \cdot u_i + u_{i-1}}{\Delta x^2} \quad (15)$$

$$\left(\frac{\partial u}{\partial x}\right)\Big|_i = u'_i \cong \frac{u_{i+1} - u_{i-1}}{2 \cdot \Delta x} \quad (16)$$

### 3.2 Variational Formulation

It is not possible to arrive directly at the diffusion equation using a variational formulation, since the first derivative vanishes when the Euler-Lagrange equation is applied to the functional. However, it is possible to asymptotically arrive to the diffusion equation by using a procedure starting with a similar equation and then making a quantity going to infinity. The following functional is then proposed:

$$I = \int_0^1 \left[ \int_0^\infty e^{-\lambda \tau} \cdot (\lambda \cdot f'(u) \cdot u_\tau^2 + \lambda^2 \cdot u_x^2) \cdot d\tau - \lambda \cdot u_x^2(x, 0) \right] \cdot x^2 \cdot dx \\ + \int_0^\infty \beta \cdot e^{-\lambda \tau} \cdot \left[ \lambda^2 \cdot (w - u(1, \tau))^2 + \lambda \cdot \frac{1}{\alpha} \cdot w_\tau^2 \right] \cdot d\tau \quad (17)$$

where  $u_x$  is the first derivative of  $u$  with respect to  $x$ ,  $u_\tau$  is the first derivative of  $u$  with respect to  $\tau$ , and  $w_\tau$  is the first derivative of  $w$  with respect to  $\tau$ .

Some asymptotic relations can be obtained for large values of  $\lambda$ . From the theory of Laplace transforms, the following equation is valid (Spiegel, 1965):

$$\int_0^\infty e^{-\lambda \tau} \cdot f(\tau) \cdot d\tau = \sum_{k=0}^{\infty} \frac{1}{\lambda^{k+1}} \cdot f^{(k)}(0) \quad (18)$$

so that Eq (17) converges to a finite value when  $\lambda \rightarrow \infty$ .

The stationary condition of a functional is given by the Euler-Lagrange equation. For an integrand ( $F$ ) that depends only on  $u, u_x, u_\tau$ , the stationary condition is:

$$-\frac{\partial F}{\partial u} + \frac{\partial}{\partial \tau} \left( \frac{\partial F}{\partial u_\tau} \right) + \frac{\partial}{\partial x} \left( \frac{\partial F}{\partial u_x} \right) = 0 \quad (19)$$

Applying this stationary condition to the proposed functional with respect to the profile  $u(x, \tau)$ , after some rearrangements, the results is:

$$\left[ -f'(u) \cdot u_\tau + \frac{1}{x^2} \cdot \frac{\partial}{\partial x} (x^2 \cdot u_x) \right] + \frac{1}{2 \cdot \lambda} \cdot [f''(u) \cdot u_\tau^2 + 2 \cdot f'(u) \cdot u_{\tau\tau}] = 0 \quad (20)$$

This is not Eq (2), but as  $\lambda \rightarrow \infty$  this equation asymptotically tends to Eq (2). Boundary condition Eq (5) is naturally satisfied, while boundary condition Eq (4) comes from the stationary condition for the term  $u(1, \tau)$ . Initial condition Eq (6) is given.

The stationary condition for the profile  $w(\tau)$  is given by:

$$-\frac{\partial F}{\partial w} + \frac{d}{d\tau} \left( \frac{\partial F}{\partial w_\tau} \right) = 0 \quad (21)$$

which, after rearrangements, leads to:

$$[w - u(1, \tau)] + \frac{1}{\alpha} \cdot w_\tau - \frac{1}{\lambda} \cdot \frac{1}{\alpha} \cdot w_{\tau\tau} = 0 \quad (22)$$

This is not Eq (3), but as  $\lambda \rightarrow \infty$  this equation asymptotically tends to Eq (3). Initial condition Eq (7) is given.

### 3.2.1 The Ritz Method - Solution with an Interpolating Polynomial

One particular application of the variational method is finding approximated solutions to differential equations, also known as the Ritz method. It consists in finding a corresponding functional that results in the differential equation, then using trial functions in the functional, and then applying the stationary conditions with respect to the parameters in the trial functions. Using Lagrangian interpolation, the following trial function is considered:

$$u(x, \tau) = \sum_{j=1}^M l_j(x) \cdot u(x_j, \tau) \quad (23)$$

where  $l_j(x)$  are the Lagrangian polynomials at some given points  $x_1, \dots, x_M$ , so that  $l_j(x_k) = 0$  for  $k \neq j$  and 1 otherwise. The trial function is then substituted into Eq (17). A Gaussian quadrature is applied, and since the integration is from  $x = 0$  to  $x = 1$ , with weight function  $x^2$ , the Gaussian integration of moments with  $k = 2$  is used (Abramowitz and Stegun, 1972). The following results will then be used:

$$\int_0^1 f'(u) \cdot u_\tau^2 \cdot x^2 \cdot dx = \sum_{j=1}^M \left[ W_j \cdot f'(u_j) \cdot \left( \frac{du_j}{d\tau} \right)^2 \right] \quad (24)$$

$$\int_0^1 u_x^2 \cdot x^2 \cdot dx = \sum_{j=1}^M \left[ W_j \cdot \left( \sum_{k=1}^M l'_k(x_j) \cdot u(x_k, \tau) \right)^2 \right] \quad (25)$$

where  $u_j = u(x_j, \tau)$  is a function of  $\tau$  at each given point  $x_j$ , and where the points  $x_j$  and the weights  $W_j$  can be found in Abramowitz and Stegun (1972) for Gaussian integration of moments with  $k = 2$  (the weight function  $x^2$  is already included in the weights  $W_j$ ).

The functional  $I$  is then given by Eq (26), where  $u_j = u(x_j, \tau)$  and  $u_{j,\tau} = du_j/d\tau$ :

$$I = \int_0^\infty e^{-\lambda\tau} \cdot \left[ \lambda \cdot \sum_{j=1}^M W_j \cdot f'(u_j) \cdot \left( \frac{du_j}{d\tau} \right)^2 + \lambda^2 \cdot \sum_{j=1}^M W_j \cdot \left( \sum_{k=1}^M l'_k(x_j) \cdot u(x_k, \tau) \right)^2 \right] \cdot d\tau \\ - \lambda \cdot \sum_{j=1}^M W_j \cdot \left( \sum_{k=1}^M l'_k(x_j) \cdot u(x_k, 0) \right)^2 + \int_0^\infty \beta \cdot e^{-\lambda\tau} \cdot \left[ \lambda^2 \cdot (w - u(1, \tau))^2 + \lambda \cdot \frac{1}{\alpha} \cdot w_\tau^2 \right] \cdot d\tau \quad (26)$$

where the value of  $u(1, \tau)$  is calculated by substituting  $x = 1$  in Eq (23), since all  $x_j \neq 1$ . Also, using the initial conditions, all  $u(x_k, 0) = 0$ , so that the corresponding term is zero.

The stationary condition for  $I$  with respect to the profiles  $u(x_j, \tau)$ , for  $j = 1, \dots, M$ , is given by:

$$-\frac{\partial F}{\partial u_j} + \frac{d}{d\tau} \left( \frac{\partial F}{\partial u_{j,\tau}} \right) = 0 \quad (27)$$

Applying this stationary condition for  $I$ , for all  $j$ , and then making the limit  $\lambda \rightarrow \infty$ , the following equation is obtained, after rearrangement:

$$W_j \cdot f'(u(x_j, \tau)) \cdot \frac{du}{d\tau}(x_j, \tau) = - \sum_{k=1}^M A_{jk} \cdot u(x_k, \tau) + \beta \cdot (w - u(1, \tau)) \cdot l_j(1) \quad (28)$$

This same equation was obtained by Guirardello (2013), using a different approach, where  $A_{jk}$  is given by:

$$A_{jk} = \sum_{i=1}^M W_i \cdot l'_j(x_i) \cdot l'_k(x_i) \quad (29)$$

Repeating the same procedure for  $w$  results in Eq (3). Finally, the set of ordinary differential equations (ODE), given by Eq (3) and Eq (28), is solved, using the initial conditions  $u(x_j, 0) = 0$  and  $w(0) = 1$ .

#### 4. Experimental Data

The experimental values used in this work were taken from Trindade (2015a), who conducted batch experiments with several adsorbents, one of them the synthetic resin Sepabeads™ SP850. This is a hydrophobic resin which showed a high selectivity for  $\gamma$ -valerolactone, while adsorbing very little glucose. It is also very porous, so that the aqueous solution can enter the macro-porous, but without the resin adsorbing the water. Therefore, this resin was found suitable for the separation of  $\gamma$ -valerolactone from the glucose solution.

The results are presented in Tables 1 and 2. These batch tests were conducted at 25 °C, with an acid pH. In the tests, the diameter of the particles was 500  $\mu\text{m}$ , and they were carried out by mixing the dry resin with the solution in the proportion of  $m_{\text{res}}/V = 0.01 \text{ g/mL}$ . Table 1 presents the results for selectivity in the adsorption, for initial concentrations of 27.2015 g/L for  $\gamma$ -valerolactone (GVL) and 66.4235 g/L for glucose (GL). It can be seen from Table 1 that adsorption of glucose and  $\gamma$ -valerolactone are not competitive for this resin. Table 2 presents the concentration in the solution.

From other tests, it was found that for  $\gamma$ -valerolactone the fitted parameters for a Langmuir type isotherm were  $q_m = 2.6366 \text{ g}_{\text{GVL}}/\text{g}_{\text{res}}$  and  $b = 0.0044 \text{ L/g}$  (Trindade, 2015a). However, in the model  $q_m$  has units of [mass solute/volume resin], so it is necessary to convert it using the density of the resin.

Table 1: Adsorbed quantities for glucose and  $\gamma$ -valerolactone by SP850.

time	$\text{g}_{\text{GL}}/\text{g}_{\text{res}}$	$\text{g}_{\text{GVL}}/\text{g}_{\text{res}}$
15 min	–	0.2056
48 h	0.0060	0.2528

'–' means too low to measure by HPLC

Table 2: Batch trials for  $\gamma$ -valerolactone adsorption by SP850.

time	$C/C_0$
0	1.0000
15 min	0.9168
48 h	0.9069

#### 5. Results and Discussion

##### 5.1 Case Study

The model was solved for a case study considering porous particles of SP850 with the following adsorption parameters:  $q_m = 2663.0 \text{ g/L}_{\text{res}}$  and  $b = 0.0044 \text{ L/g}$ . The conditions for the solution and resin in the stirred tank were:  $V = 10 \text{ mL}$ ,  $v = 0.209 \text{ mL}$ , and  $C_0 = 27.2015 \text{ g/L}$ . The porosity of the particles was  $\varepsilon = 0.526$ . Also, the spheres radius was  $R = 250 \mu\text{m}$  ( $d_p = 500 \mu\text{m}$ ). These values were used to reproduce the conditions of the experimental tests ( $m_{\text{res}} = \rho_{\text{res}} \cdot v \cdot (1 - \varepsilon) = 0.1 \text{ g}$  and  $q_m[\text{by volume resin}] = \rho_{\text{res}} \cdot q_m[\text{by mass resin}]$ ).

The value of  $k_f = 1.7 \cdot 10^{-5} \text{ m/s}$  was estimated from the correlation of Geankoplis for particles in stirred tanks (Geankoplis, 1983, apud Skidmore et al, 1990), using the molecular diffusion coefficient of GVL in water which was estimated as  $D_{AB} = 1.03 \cdot 10^{-9} \text{ m}^2/\text{s}$  with the correlation of Othmer and Thakar for dilute aqueous systems (Sherwood et al, 1975).

##### 5.2 Results

The variational method was solved for  $M=3$  and  $M=5$  (3 and 5 points, respectively), and the resulting ODE system was solved with a 4<sup>th</sup> order Runge-Kutta method, with  $\Delta t = 0.01 \text{ min}$ . The finite difference method was solved with 5 and 10 intervals (6 and 11 points, respectively), and the resulting ODE system was also solved with a 4<sup>th</sup> order Runge-Kutta method, with  $\Delta t = 0.01 \text{ min}$ . The results for the dimensionless concentration in the solution ( $w$ ) are presented in Table 3, where it can be seen a good agreement between the two methods.

It is important to point out that some care must be taken with respect to the time interval  $\Delta t$ . Parabolic PDEs as Eq (2) may result in a stiff ODE system when a discretization is applied in the  $x$  domain.

Table 3: Results for the dimensionless concentration in the solution ( $w$ ) for the case study.

Time (min)	$\tau$	Variational (M=3)	Variational (M=5)	Finite Diff. ( $\Delta x = 0.2$ )	Finite Diff. ( $\Delta x = 0.1$ )
0.00	0.0000	1.0000	1.0000	1.0000	1.0000
5.00	0.3600	0.9446	0.9434	0.9451	0.9439
10.00	0.7200	0.9274	0.9268	0.9280	0.9271
15.00	1.0800	0.9172	0.9169	0.9178	0.9171
20.00	1.4400	0.9105	0.9104	0.9111	0.9105
25.00	1.8000	0.9059	0.9059	0.9065	0.9060
30.00	2.1600	0.9028	0.9028	0.9033	0.9030
$\infty$	$\infty$	0.8962	0.8962	0.8962	0.8962

The value of  $D = 7.5 \cdot 10^{-11} \text{ m}^2/\text{s}$  was fitted to reproduce the experimental values in Table 2. However, there is a difference at equilibrium,  $w_\infty = 0.8962$ , which is due to the experiments had used dry resin at  $t = 0$ , while the model implicitly assumes a wet resin at  $t = 0$  ( $c = 0$  means no solute, but the solvent is inside the pores in the model). This affects the mass balance. The calculated value at equilibrium, considering dry resin at  $t = 0$ , is  $w_\infty = 0.9052$ , which is closer to the experimental value in Table 2. One way to solve this is to use  $V^*$ , such that  $V^* = V - v \cdot \varepsilon$ , and  $c \neq 0$  at  $t = 0$  (but  $c_0 \neq C_0$ , due to  $q_0$ ), to compare experimental and simulated values.

## 6. Conclusions

The numerical methods used were able to give reliable results to represent the adsorption of GVL into spheres of SP850 resin. This resin is very selective to separate GVL from a solution of glucose. Therefore, the model and the numerical methods studied here can be used to design a better separation process using adsorption. The fitted diffusion coefficient inside the particles,  $D$ , lead to the dimensionless number  $k_f \cdot R/D = 56.67$ , indicating that for this case study the internal resistance for mass transfer is much higher than the external resistance. The value of  $D$  can then be used in other systems, since it is a parameter inside the particles, for example a fixed bed column, but then the value of  $k_f$  may be different from the one in a stirred tank.

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