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Model of a Heavy Metal Adsorption System Using the S-Layer of *Bacillus sphaericus*

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Abstract: A bidimensional and pseudo homogenous model is proposed for the study of mass transfer in the bioadsorption process of chromium VI in the S-layer of immobilized *Bacillus sphaericus*. The process takes place in a packed column. The implementation of such model in COMSOL Multiphysics is explained in detail and the final results are presented. These include chromium concentration profiles along the column and its variation with time. A parametric analysis is performed in order to show the effect that changes on both diffusivity and liquid layer mass transfer coefficients have on the column's behavior. The changes with varying charge and particle size are also investigated showing that this last one is determinant for the process.

Keywords: COMSOL Multiphysics, Adsorption, *Bacillus sphaericus*, Chromium

1. Introduction

Heavy metals from industrial activities have become a real threat for a big number of ecosystems, animals and human health (Chieh-Chen Huang et al, 2006). Among these metals, hexavalent chromium Cr(VI) has gained special significance because of its important health impacts. When dissolved in water, Cr(VI) is extremely carcinogenic and may cause death to animals and humans if ingested in large doses (Ramsay et al, n.d). Chromium is frequently employed in metal industries, paint and pigment production, wood treatments, paper manufacture among many other (Ramsay et al, n.d). These uses result in chromium discharges into lakes and rivers and eventually may lead to high Cr(VI) concentrations in underground waters. In India, for example, the total chromium discharge was calculated to be around 3,200 tons per year in 1997 (Ramsay et al, n.d) and in the United States concentrations of up to 14,600 mg/kg have been reported on some underground waters (Zayed and Terry, 2003). In Colombia, the toxicological center of the Health Secretariat of Bogota has reported a high number of heavy metals poisoning cases including poisoning due to chromium ingestion. The Environmental Epidemiological Surveillance System (Sisvea in Spanish) included this metal among the prioritized chemical species (SISVEA, 2009). Leather tanning industries are the most common chromium sources in Bogota and these have their main process plants at the Tunjuelito river shore (García, 2008).

Bioremediation is a type of technology that uses metabolic processes of micro-organisms in order to degrade or transform pollutants in a way that may be in a non threatening state for the environment or public health (Ramsay et al, n.d). The GDPP and the CIMIC at Universidad de los Andes are working on the removal of the hexavalent chromium in water using an adsorption column with immobilized *Bacillus sphaericus* and have a good number of experimental projects related to this topic. This work is framed in this research project and it aims to develop a model using COMSOL Multiphysics of the Cr(VI) adsorption process in a column.

Some mathematical models similar to the one presented here have been proposed but their results have not been conclusive or have been developed for different systems, making it hard to rely on them for future research. For instance, García (2008) worked on the Cr(VI) transfer and attempted to compare her results to the experimental evidence of the time but the results were not conclusive.

2. Theory and governing equations

Commonly, adsorption models concerning packed columns consider three different mass transfer stages before the adsorption actually takes place:

a. Mass transfer between particles. This stage considers the diffusion and advection of chromium in the water surrounding the *B. sphaericus* particles. This stage is very

important in the modeling of the process due to the relative movement between the water passing through the column and the immobilized bacteria.

b. Mass transfer at the interface. This stage accounts for the mass transfer between the bulk fluid and the water-packing interface.
c. Mass transfer within the solid particles. Chromium may then diffuse inside the pellet's pores or even at its surface.

To account for these effects a single porosity model is frequently used. This model assumes an isothermal process and the mass balance equation for the solute is described as follows:

$$\varepsilon_e \frac{\partial C_i}{\partial t} + \rho_p(1-\varepsilon_e)\frac{\partial \bar{q}_i}{\partial x} + \varepsilon_e \frac{\partial (u.C_i)}{\partial z} = \varepsilon_e(E + D_m)\frac{\partial^2 C_i}{\partial z^2} \quad (1)$$

Where ε_e is the pellets porosity, C_i is the chromium concentration in the water, ρ_p is the particle's density, q_i is the adsorbed chromium concentration, u is the flow's velocity in axial direction, D_m is the diffusivity coefficient and E is the axial dispersion coefficient.

The first and last terms of the LHS of equation (1) refer to a possible chromium accumulation in the solution and to the dispersion due to movement of the fluid respectively, each with an additional term that accounts for the pellet's porosity. The second term accounts for the accumulation of adsorbed chromium inside the column. The term on the RHS of equation (1) refers to axial dispersion and diffusion. Note that the equation makes reference to a one-dimensional model so it needs some adjustments in order to model a possible diffusion in the radial direction. These adjustments are simple to include when using COMSOL Multiphysics thanks to the possibility of setting a two-dimensional model from the beginning of the modeling process.

Assuming that the chromium in the pores is in equilibrium we can describe the mass transfer through the liquid film using equation (2) as shown below.

$$\rho(1-\varepsilon_e)\frac{\partial \bar{q}_i}{\partial t} = K_m a_p [C_i - C_i^*] \quad (2)$$

Where K_m, a_p and C_i^* are the matter coefficient for the liquid film, the external surface area by unit volume, and the chromium equilibrium concentration in the solution respectively. The equilibrium concentration C_i^* may be related to q_i using the equation of Langmuir's isotherm for the process. This equation is shown below (Equation 3) and defines the equilibrium state in the pores.

$$q_i = \frac{QC_i^*}{k + C_i^*} \quad (3)$$

This model assumes the following besides the isothermal process mentioned earlier (García, 2008):

- The solid particles (immobilized bacteria) may be modeled as spheres.
- The total resistance for mass transfer may be expressed as a linear combination of individual resistances.
- The packing is homogeneous.
- There is no radial concentration gradient
- There is no phase change or chemical reaction besides the adsorption process.
- The presence of free cells inside the column is negligible.

All the preceding equations are to be solved simultaneously in order to find the concentration profile for the chromium in the solution and the one adsorbed.

3. Use of COMSOL Multiphysics

When setting up the model in COMSOL Multiphysics it is important to follow four basic steps, namely: creation of the geometry, definition of physical laws and equations of the model, mesh generation and running the solution of the model.

3.1 Creation of the geometry

The process will take place in a cylindrical column so the creation of the geometry is quite straight forward. The system will be represented by a rectangle as tall as the column and width equivalent to the column's diameter.

3.2 Definition of physical laws and equations

The Chemical Engineering module (COMSOL Multiphysics, 2007a) was chosen for this modeling exercise. In the mass transfer mode, COMSOL Multiphysics allows the user to work with the general mass transfer equation which is shown below (Equation 4). The user must provide the numerical values or expressions for the constants in the model such as dispersion coefficients.

$$\delta \frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = R_i - u\nabla \cdot c_i \quad (4)$$

In equation (4) the first term of the LHS refers to the accumulation in the system and the second term accounts for the diffusion that may take place in any direction. On the RHS of equation (4) the first term is a chemical reaction term and the other one accounts for any convection process in the system. Note that the system to be modeled has no reaction. However, the reaction term can be used to account for the adsorption if the change of phase is considered as a reaction that transforms chromium from a dissolved state into an adsorbed state. Table 1 relates the COMSOL coefficients in equation (4) with the equivalent term in our model defined by equations (1) through (3). Having in mind that there are two different chromium phases (or "species") we will need a set of expressions for each one.

Table 1: Coefficients in equation 4 and equivalent in equations 1 through 3

Coefficient	Expression C_i	Expression q_i
δ	ε_e	$\rho_p(1-\varepsilon_e)$
D_i	$\varepsilon_e(E+D_m)$	0
u	ε_e*u	0
R_i	$-K_f*a_p(C_i-C_i*)$	$K_f*a_p(C_i-C_i*)$

3.3 Mesh generation

The generation of an appropriate mesh is very important in order to achieve accurate results without unnecessary computational demand. For two-dimensional problems with simple geometries like the one presented here, the mesh will consist of small triangles that can have up to seven nodes each. The solution will use degree 5 polynomials maximum so the central node will not be necessary. COMSOL may generate the mesh automatically but in this case, given the difference in scale between the column's height and radius it is important to include an additional discretization parameter in the radial direction in order to improve the accuracy of the result. This parameter was set to 2000% (COMSOL Multiphysics, 2007b).

3.4 Running the solution

The solution is based on a finite element solution algorithm. Once the elements are defined on the previous step, the concentration values for each node will be estimated using a polynomial expression. Note that in order to obtain more precise results two different approaches can be used: 1) Increase the number of elements in the mesh or 2) increase the polynomials' degree. Some previous work done by Desai and Abel (1972) suggests that it is normally more fruitful to use the second approach, so for the solution of equations 1 through 3, polynomials of up to degree 3 were used.

It is crucial to specify from the beginning that the model is time-dependant in order to be able to see how the column's concentration varies as the process takes place. When using this method, time limits and time steps have to be defined. However, note that these steps are only used for post-processing purposes. The time step for solving the equations is defined independently. Specific and absolute tolerances will also have to be defined in this step.

4. Results

Figure 1 shows the concentration profile obtained when using a 1 ml/min flow and a immobilized pellet surface area of 1.57cm^3. These conditions where set according to the experimental method developed by Florez (2008). As can be seen from Figure 1, the experimental results reported by Florez adjust well to the results predicted by the model. However, it is important to have in mind that the parameters D_m and K_m were defined in a way that their value would minimize the error because there is no experimental data to obtain such values.

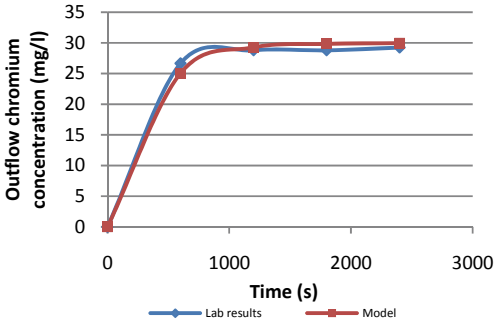

Figure 1. Comparison between the model and experimental profiles using a 1ml/min flow and 0.5x0.5x0.5 pellets. The experimental results are reported by Florez (2008).

Florez's experimental work includes results for the column operating at different loading and particle size conditions. Figure 2 shows how these results correlate to the ones predicted by the model for two different initial conditions. This time the values for D_m and K_m were left constant.

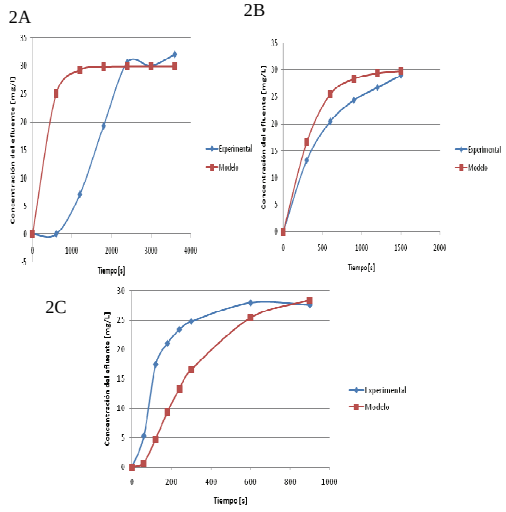

Figure 2. Comparison between experimental and the model results. 2A is for a 1ml/min flow and 1x1x1 pellets. 2B shows the results for a 2ml/min flow and 1x1x1 pellets. 2C is for 2ml/min and 0.5x0.5x0.5 pellets.

Note that the general behavior and the saturation point of the model are consistent with the experimental results. However, there are important differences between the model's results and the experimental observations at the beginning of the process.

Figure 3 shows the evolution of concentrations along the column. The x-axis shows the distance along the diameter of column in meters and the y-axis shows the distance along the principal axis of the column. Next to each image, a color scale is shown to indicate the equivalent concentration value according to the color shown. The last image shows how after 2040 seconds the whole column is at the same chromium concentration as the inflow so no effective mass transport takes place.

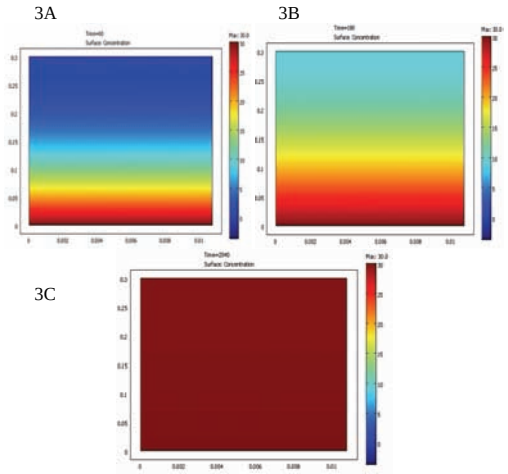

Figure 3. Evolution of the chromium concentration profile. 3A, 3B and 3C show the results after 60, 180 and 2040 seconds respectively.

5. Discussion

In this model there are two parameters that can be adjusted to improve the results predicted. These are the diffusivity coefficient (D_m) and the matter coefficient for the liquid film (K_m). Figures 4 and 5 show the effects that changing such parameters have on the concentration profile. Note the diffusivity coefficient has a direct effect on the column's saturation time. This behavior is as expected having in mind that a smaller D_m will make the diffusion process take longer, making the hole system less efficient.

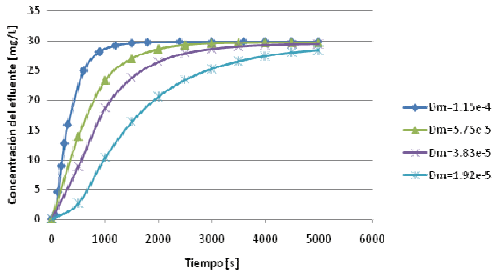

Figure 4. Analysis of the behavior for different values of D_m

On the other hand, the changes in the matter coefficient for the liquid film result in a reduction in the column's saturation concentration. In other words, when K_m is to high the ability of the system to adsorb chromium will be reduced due to an early chromium saturation of the pellets.

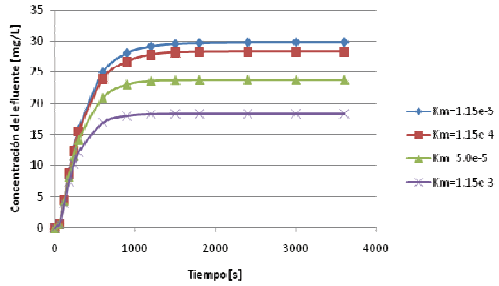

Figure 5. Analysis of the behavior for different values of K_m

Another important result to comment is the lack of a radial dispersion profile. As can be seen from Figure 3, the changes in concentration are always along the main axis of the column. This is probably due to the small column radius that makes any concentration or velocity profiles negligible in this direction. These results justify a plug flow approach for future investigations.

Florez (2008) mentions in her work that the particle size has a bigger impact on the mass transfer than the inflow speed. The results obtained from this model suggest a similar conclusion. When the particle size is varied but the inflow speed is kept the same, the variation is normally greater than when the pellet's size is kept constant. Table 2 shows the sum of the squared differences (SSD) between the results when using an inflow speed of 1ml/min and pellets of 1x1x1 and then using a 1ml/min speed and 0.5x0.5x0.5 pellets (second line in the table) or 2ml/min with 1x1x1 pellets (third line). As in Florez's results, the difference when the particle size is changed is greater than when the inflow speed is changed.

Table 2: Sum of the squared differences when changing particle size and velocity of flow

Change	SSD
Particle size	1.75
Velocity	1.56

This suggests that the process is limited by the pellet size and in a lesser extent by the inflow speed. However, when these changes are modeled, the effect is seen on the saturation level and not on the saturation time as suggested by the experimental results. This effect is easily explained when looking back at equations 1 through 3 where it can be noted that a change in the pellet's surface area will only affect K_m and not D_m. The experimental results thus suggest that there is a relationship between the surface area and the diffusivity coefficient that the model does not consider. This relationship is left for future research.

6. Conclusions

A Cr (VI) adsorption column was modeled using COMSOL Multiphysics. The model is pseudo homogeneous and includes axial and radial dispersion terms. The solutions studied adjust well to experimental results developed previously on a column using immobilized *Bacillus sphaericus* pellets and suggest that particle size has a greater influence on the mass transfer process than the inflow speed, just as experimental observations imply. It was demonstrated that radial diffusivity is negligible, validating a plug flow approach.

7. References

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