A Numerical Simulation of Adsorption Using Non-Standard Isotherm Equations in COMSOL

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Abstract: An array of numerical simulations of the equation of transport were performed using the adsorption isotherm equation proposed by Zhu and Gu, and a simple cubic polynomial. The COMSOL implementation, was in 1D, where the solutes are injected from one face of a homogeneous, isotropic core (small sample of reservoir rock); the concentration of the injected surfactant is kept constant during all the simulation. The spatial distribution of the adsorption of solutes along the rock core was investigated. The main idea is to attempt to understand the numerical effects of varying several features of the modeling of the transport equation.

Keywords: Adsorption isotherms, mathematical modeling, transport in porous media, surfactants, asphaltenes.

1. Introduction

Adsorption occurs whenever a solid surface is exposed to a gas or liquid: it is defined as the enrichment of material or increase in the density of the fluid in the vicinity of an interface [1]. Adsorption in porous media (like a reservoir), is important since the solutes potentially adsorbable (adsorptives) may actually become adsorbed (thus becoming adsorbates), and thus they may change some of the rock properties, particularly those important for defining the flow of fluids within them, e. g. the reduction in porosity due to adsorbates may change the permeability significantly [1].

In the case of adsorption from solution, the ‘apparent adsorption’ of a solute at the liquid-solid interface is usually evaluated by measuring the decrease in its concentration when brought into contact with the adsorbent. The adsorption isotherm is then plotted as the apparent adsorption of the solute against the equilibrium concentration at a known temperature [1]; experimentally, the setting may be an array of vases with the same proportion of rock mineral with respect to an added solution. The concentration of solute for each vase is varied, and after some time, it is measured the amount of adsorbed material onto the rock [2], thus a collection of experimental data is obtained, which then may be fitted to a suitable adsorption isotherm formula.

What makes an isotherm formula ‘suitable’ depends very much on the physical and/or chemical assumptions that would suggest the pattern of adsorption being followed by the adsorptive onto the porous media [1]. Hence, such chosen formula renders upon fitting a collection of parameters which might have a particular interpretation, making the isotherm useful or not.

The implementation of a numerical model into a program like COMSOL may require the knowledge of the limitations such program may face, depending on the parameters being input, e.g. the *global* and *local* Péclet number, as it will be shown.

1.1 Zhu and Gu Isotherm equation

The formula of Zhu and Gu [2] is meant to be for certain type of micelles (molecular aggregates with two extremes, each of different chemical affinity [3]), which in turn have some convenient clustering properties, since some assumptions may be made, so that the following equation is being rendered:

$$\Gamma = \frac{\Gamma_\infty k_1 C \left(\frac{1}{n} + k_2 C^{n-1} \right)}{1 + k_1 C \left(1 + k_2 C^{n-1} \right)} \qquad (1)$$

Where Γ is the adsorption as a function of the concentration C; Γ_∞ is the maximal amount of adsorbed substance (adsorbate) onto an adsorbent (for example onto a porous media, like a rock); k_1 is a constant related to the first adsorption step (e.g., first layer of bulk molecules onto the rock surface); k_2 is related with the subsequent layers adsorbed (e.g. layers of molecules one over another); and n is the aggregation number. Eq. (1) has been used to describe the behavior of adsorption of surfactants (substances that change wettability [3]) onto asphaltenes [4]. For most of the simulations, it was taken the fitted data of the surfactant NPE6 [4]: $\Gamma_\infty = 0.00053$, $k_1 = 1800$, $k_2 = 6.5\times10^{20}$, $n = 20$.

1.2 Cubic model

For comparison, a cubic polynomial (a purely mathematical equation, without a direct physical interpretation) of the form

$$\Gamma = a_1C + a_2C^2 + a_3C^3 \qquad (2)$$

was also fitted, and simulations were carried on using this simplistic formula as well (Fig. 1).

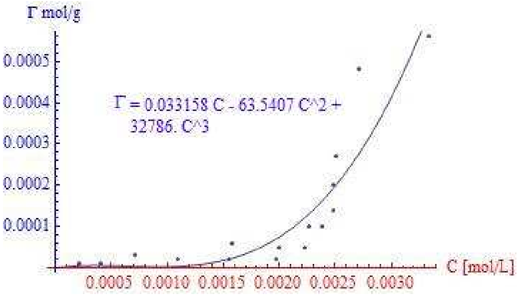

Figure 1. Cubic polynomial (blue line), fitting experimental data for the surfactant NPE6 to form a simplistic “isotherm”.

It was noticed in [4] that some of the experimental data, did not fit so ‘tightly’ to Eq. (1), since the Zhu & Gu equation suggests the an asymptote, which is not clearly supported for most of the surfactants tested in [4], with the exception of NPE6, the data of which is shown in Fig. 1. The data suggest at single glance the possibility of fitting a cubic polynomial. On the other hand, Eq. (1) is a highly non-linear equation, so presumably a cubic polynomial should run much faster.

2. Systematic Modelling

In order to implement an appropriate mathematical model of the transport and adsorption of adsorbates, usage has been made of the systematic modeling equation of continuous media [5]:

$$\partial_t\psi_\gamma^\alpha + \nabla\cdot(\psi_\gamma^\alpha \vec{\mathrm{v}}^\alpha - \vec{\tau}_\gamma^\alpha) = g_\gamma^\alpha ; \forall \vec{x} \in B(t) \qquad (3)$$

Where ψ_γ^α is an intensive property (mass density ρ times the porosity ϕ in our case), linked to the γ component of the α phase; $\vec{\mathrm{v}}^\alpha$ is the average phase velocity, which it is assumed to be the Darcy velocity $\vec{u}^\alpha \equiv \phi^\alpha\vec{\mathrm{v}}^\alpha$; $\vec{\tau}_\gamma^\alpha$ is the flow of the property through the boundaries of the system, linked to the γ component of the α phase, which in our case is a generalized Fick law $\vec{\tau}_\gamma^\alpha = \vec{\vec{D}}^\alpha\cdot\nabla\psi_\gamma^\alpha$, where $\vec{\vec{D}}^\alpha$ is the tensor of hydrodynamic dispersion, which includes dispersivity and the molecular diffusion; g_γ^α represents possible sources inside the body $B(t)$. Table 1 summarizes the properties and components used for this work

Table 1. Intensive properties corresponding to each component of the transport equation being considered.

Phase	Compon-ent	$\int_V \psi_\gamma^\alpha dV$ (Extensi-ve property = mass)	“Intensi-ve” Property ψ_γ^α
Water $\alpha = w$	Water $\gamma = w$ Solute $\gamma = s$	$M^w(t)$ $M_s^w(t)$	$\phi\rho^w$ ϕc_s^w
Rock $\alpha = r$	Rock $\gamma = r$ Solute $\gamma = s$	$M^r(t)$ $M_s^r(t)$	$\rho_b^r =$ $(1-\phi)\rho_p^r$ $(1-\phi)c_s^r$

Making the appropriate substitutions from Table 1 on Eq. (3), we arrive to the transport equation for the adsorbates, in water

$$\begin{aligned}&\partial_t(\phi c_s^w) + \\ &+\nabla\cdot\left(\vec{u}c_s^w - \vec{\vec{D}}^w\cdot\nabla(\phi c_s^w)\right) = g_s^w\end{aligned} \qquad (4)$$

And in the rock

$$\partial_t\left((1-\phi)c_s^r\right) = g_s^r = -g_s^w \qquad (5)$$

The “transport” equation of water

$$\partial_t(\phi\rho^w) + \nabla\cdot(\rho^w\vec{u}) = 0 \qquad (6)$$

And finally the “transport” equation for the rock

$$\partial_t\left((1-\phi)\rho_p^r\right) = 0 \qquad (7)$$

Eqs. (5) and (6) may be combined to form a single one:

$$\begin{aligned}&\partial_t\left(\phi c_s^w + (1-\phi)c_s^r\right) + \\ &+\nabla\cdot\left(\vec{u}c_s^w - \vec{D}^w\cdot\nabla\left(\phi c_s^w\right)\right) = 0\end{aligned} \qquad (8)$$

If the movement of the adsorbate is slow, compared with the adsorption rate, then we may assume this last to be of controlled-equilibrium [6], which implies that adsorption depends on the concentration of flowing adsorbate, and in turn this allows the mathematical chain rule to be applied as follows:

$$\partial_t c_s^r = \partial_{c_s^w} c_s^r \partial_t c_s^w \qquad (9)$$

Where $\partial_{c_s^w} c_s^r$ is the slope of the isotherm. Therefore Eq. 9 is rendered as

$$\begin{aligned}&\left(\phi + (1-\phi)\partial_{c_s^w} c_s^r\right)\partial_t c_s^w + \\ &+\nabla\cdot\left(\vec{u}c_s^w - \vec{D}^w\cdot\nabla\left(\phi c_s^w\right)\right) = 0\end{aligned} \qquad (10)$$

Furthermore, dividing by the porosity

$$R_F \partial_t c_s^w + \nabla\cdot\left(\vec{v}c_s^w - \vec{D}^w\cdot\nabla c_s^w\right) = 0 \qquad (11)$$

Where

$$R_F \equiv \left(1 + \left(\frac{1-\phi}{\phi}\right)\partial_{c_s^w} c_s^r\right) \qquad (12)$$

is the *retardation factor*, and now $\vec{v}$ is the pore velocity. Eq. (11) is the transport equation being modeled in COMSOL. The initial and boundary conditions are

$$c_s^w(x, t=0) = 0 \qquad (13)$$

$$c_s^w(x=0, t) = c_{s\ iny}^w \qquad (14)$$

(*iny*=inyected; Dirichlet)

$$\nabla_x c_s^w\big|_{x=L} = 0 \text{ (Neumann)} \qquad (15)$$

Apart from the parameters of the isotherms, mentioned in the introduction, the following constants were established for the coefficients of the transport equations:

$$\phi = 0.2295$$

$$|\vec{v}| \in \left\{10^{-4}, 10^{-3}, 10^{-2}\right\} \text{ m/s}$$

$$L = 0.25 \text{ m}$$

$$D \in \left\{10^{-7}, 10^{-6}, 10^{-5}\right\} \text{ m}^2\text{/s}$$

$$c_{s\ iny}^w \in \left\{0.0005\times j, 1 \le j \le 7\right\} \text{mol/L}$$

$$t \in \left\{20, 180, 12000, 86400\times 100\right\} \text{s}$$

The values of the parameters were chosen so that a wide numerical "sweeping" could be performed, and thus, investigate several important numerical behaviors. So, for example, the injected concentration was varied according to the different parts of the isotherm of NPE6, i.e. the beginning, the rise and the asymptotic part of the isotherm.

3. COMSOL Implementation

The implementation of Eq. 11 in COMSOL was done in the PDE, coefficient mode. For most of the simulations it was used quadratic Lagrange elements, although couple of them where performed with cubic Hermite elements, with no significant differences. Most of the simulations used a mesh of 240 elements, and it was also swept in some of them from 15 to 240, in order to see the change in the numerical behavior.

It was also attempted to implement Eq. 11 using the Earth Science module of COMSOL, but at least with the parameters being used simulations ran very slow, so unfortunately no comparison can be shown at the moment of both modes. It is suspected that the slowness in the Earth Science module might have to do with the high density of the mineral being used in the simulations (Berea sandstone, 2.1 g/m^3, or 20.1 mol/L).

4. Results and discussion

4.1 Péclet number

The global Péclet number [7] is taken here as

$$Pe = \frac{LV}{D} \qquad (16)$$

where L is the length of the system, V is the input velocity, and D is the diffusion. The *local* Péclet number, in a one-dimensional system, and with uniform mesh, depends on the number of elements, so

$$Pe_{local} = \frac{(L \div \#elements)V}{D} \qquad (17)$$

It is known that if the Péclet number is higher than one, then there is a dominating advection, thus leading to numerical errors [7], and the size of the mesh must be lowered, or the number of elements must be increased. Such behavior was indeed observed, and the Péclet number it the simulations of this work varied from 2.5 up to 2500, being 25 the most common. A mesh size of 240 elements, with 481 degrees of freedom, rendered quite reasonable results in most cases.

4.2 Accumulation due to velocity

Using a diffusion of 10^{-6}, a velocity of 10^{-2}, with $c^{w}_{s\ iny} = 0.0005$ and for a simulation of 180s, it was observed inside the system an increase of concentration, which is believed to be an accumulation of surfactant around the point of 0.7m from the inlet (Fig. 2)

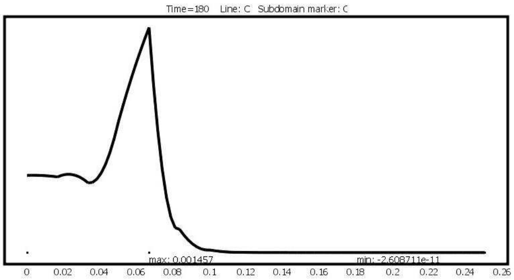

Figure 2. Possible "accumulation" due to velocity at 0.07 m.

4.3 Dependence of simulation time with injected concentration

In general it was observed that the higher the concentration being used, the longer the system it took to be solved (Fig. 3).

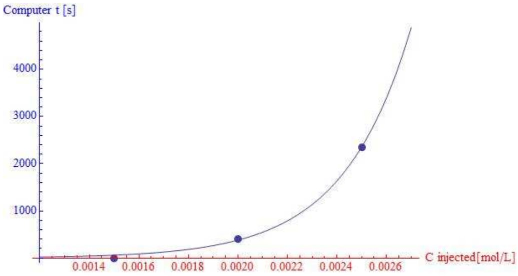

Figure 3. Exponential growth of simulation for 20 simulation seconds.

So for example, an injected concentration of 0.0005 mol/L, could be ran for 12000 s of simulation, in less than 1 second (Fig. 4)

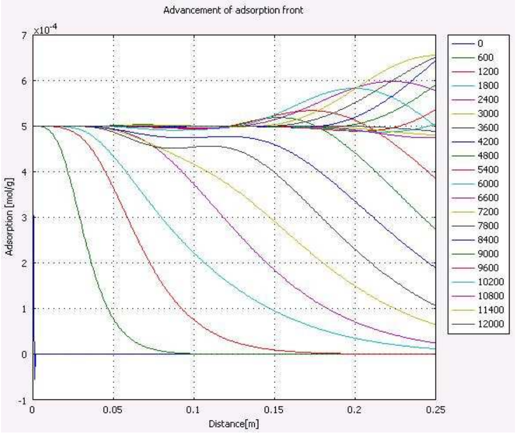

Figure 4. The advancement of the adsorption front inside the system took a simulation time of around 12000 s for an injected concentration of 0.0005 mol/L.

Higher concentrations would simply take a very long computer time to be performed, and still sometimes rendered numerical errors, in spite of using a finer mesh; negative concentrations were observed in the last cases, for example. Presumably this phenomenon, in all likelihood, could be attributed to the high non-linearity of Eq. (1).

4.4 Improvement of computer time through the cubic model

This was the point where it was thought that one way for speeding the simulations could be attained by replacing the isotherm formula of Eq. (1), using the simpler polynomial of Eq. (2). It is granted that this polynomial does not have a physical interpretation (for the moment), but as it was mentioned before, since there the experimental data only weakly supports the possible existence of the asymptotic part of Eq. (1), then for the time being the cubic polynomial did make the simulations run much faster, so for example, the highest concentration being considered (0.0035 mol/L) of injected surfactant, could be simulated for a simulation time of 100 days in less than one second. Fig. 5 shows how under these conditions, the surfactant almost exits the porous media through the right end.

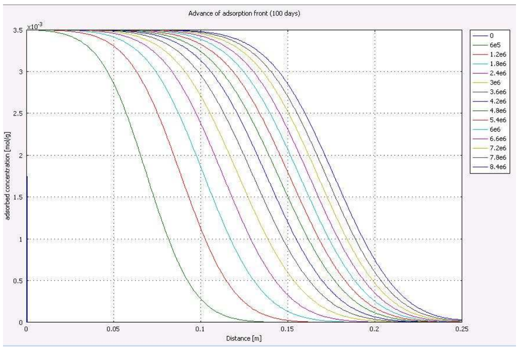

Figure 5. Advance of adsorption front inside the system, using a cubic polynomial as an adsorption isotherm. In 100 days the surfactant has advanced almost through the entire length of the system.

4. Conclusions

High Péclet numbers were obtained, signaling for some possible numerical issues, that should be considered in future simulations. The increase of velocity seemed to produce possible accumulation points almost at the beginning of the system. The higher the injected concentration, the longer the computer time and actually was increasing exponentially, possibly because the high non-linearity of the Zhu & Gu equation. A cubic polynomial was used for much faster simulations, in the case of the highest concentrations, and even when very long simulation times were being considered. In future works, comparisons of performance between the Earth Science module, and the PDE coefficient form module are expected.

5. References

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6. Acknowledgements

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