

Modelling the H₂S adsorption from biogas with COMSOL Multiphysics®

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Abstract

Biogas represents one of the most promising renewable sources for energy production, in which the livestock manure provides several key advantages for the anaerobic biodigestion process. However, desulfurization is necessary to prevent corrosive mechanisms and protect the system from hydrogen sulfide (H₂S). The adsorption of H₂S onto activated carbon is one of the most widely used methods, which is generally set up and investigated in a fixed-bed column, where it is also possible to measure the breakthrough curves and the adsorption capacity of the adsorbents.

In this work we develop a two-dimensional, axisymmetric, time-dependent model of H₂S adsorption in a fixed-bed column. The physical model consists of a porous bed of packed spherical particles, through which a mixture of methane, carbon dioxide, and hydrogen sulfide enters. In COMSOL Multiphysics® we describe the gas flow by the Brinkman Equations interface for porous media, whereas the Transport of Diluted Species in Porous Catalysts interface accounts for the evolution of the species by diffusion, convection and mass transfer mechanisms. For the adsorption process, the mass transfer in the fluid inside the porous matrix is treated by means of a Linear Driving Force (LDF) model. On the other hand, the adsorption of H₂S onto the porous particles is modeled using both the Langmuir and Freundlich nonlinear isotherms. Some parameters of the model representing the kinetics of the adsorption process have been selected from the literature, whereas other values have been estimated by empirical correlations. The computational results describe satisfactorily the adsorption process of H₂S from biogas, showing the influence of the main operational parameters. The evolution of the mass transfer zone in the porous fixed-bed column is also well characterized, as well as its progression along the length of the reactor. The breakthrough curves simulated by the model indicate favorable kinetics and bed efficiencies.

Keywords: biogas, H₂S adsorption, fixed bed porous reactor, breakthrough curve, computational modelling.

1. Introduction

Biogas represents one of the most promising renewable sources for energy production, in which the livestock manure provides several key advantages for the anaerobic bio digestion process [1]. However, desulfurization is necessary to prevent corrosive mechanisms and protect the system from hydrogen sulfide (H₂S), an undesirable gas which is also toxic and flammable. Among the different conventional techniques used to purify biogas, adsorption is a preferable solution due to its cost-effectiveness, ease of implementation and ability to operate at ambient temperature and pressure [2]. The affinity of a gas component (adsorbate) for a particular adsorbent depends on molecular properties such as size, shape, polarity, its partial pressure or concentration and temperature, and is controlled by van der Waals forces and hydrophobic interactions [3]. For the purification of biogas, the adsorption of H₂S onto activated carbon is one of the most widely used methods [4], which is generally set up and investigated in a fixed-bed column, where it is also possible to measure the breakthrough curves and the adsorption capacity of the adsorbents.

Interesting works have been developed in the past to describe the behavior of a fixed-bed adsorber using computational modelling. Gutierrez et al. [5] studied the adsorption of hydrogen sulfide from biogas on treated sewage-sludge, first using the analytical solution of the Bohart and Adams equation. Next the authors based their work on the linear driving force (LDF) model and carried out a numerical solution with the aid of the Aspen Adsorption™ software. The same authors (Aguilera and Gutierrez [6]) continued their efforts to model the fixed-bed breakthrough curves for H₂S adsorption from biogas, this time incorporating an axially dispersed plug flow with a non-linear isotherm based on the LDF approximation. The numerical solution obtained using COMSOL Multiphysics® revealed that the overall mass transfer coefficient of the LDF model was underestimated when axial dispersion was neglected. Moreover, the computational results reported in [6] matched well the experimental results, especially with the Freundlich isotherm if compared to the Langmuir isotherm. An interesting review of mathematical modelling of fixed-bed columns to adsorb carbon dioxide emissions has been published by Shafeeyan et al. [7]. In this work the authors reviewed various gas-solid equilibrium

relationships as well as different descriptions of the mass transfer mechanisms within the adsorbent particles. COMSOL Multiphysics® was applied by the same authors [8] to solve the coupled differential equations which modelled the carbon dioxide adsorption onto ammonia-modified activated carbon and in [9] to study the H₂S catalytic oxidation in an impregnated activated carbon (IAC) packed bed reactor (PBR). Papurello et al. [10] analyzed computationally the performance of IAC for the removal of H₂S from sewage biogas and evaluated the effect of several operating parameters on adsorption capacity using a Langmuir experimental curve. A numerical simulation of the desulfurization of gas streams by adsorption method has been developed by Lobo dos Santos et al. [11], using an approach like [6] which permitted a very careful analysis of the mass transfer zone (MTZ) and breakthrough curves in the reactor. Finally, Bareschino et al. [12] studied and modelled in COMSOL Multiphysics® the H₂S adsorption from a synthetic biogas mixture onto zeolite. They proposed a one-dimensional coupled heat and mass transfer model based on the LDF approximation, accounting for H₂S oxidation and deactivation of zeolite due to sulfur deposited in its pores.

In this work we develop a two-dimensional, axisymmetric, time-dependent model of H₂S adsorption in a fixed-bed column, following the work of Aguilera and Gutierrez [6] and using their experimental data required to describe the equilibrium isotherm of the adsorption mechanism. The structure of the paper is as follows. The description of the physical model and the governing equations are given in Section 2. The computational results are presented and discussed in Section 3. Finally, Section 4 summarizes the main conclusions of the work.

2. Model of the biogas adsorption

2.1. Physical model

The porous medium (see [13] for some definitions) model consists of a bed of packed spherical particles, through which a mixture of methane, carbon dioxide, and hydrogen sulfide enters. A schematic of the porous fixed bed column is depicted in Fig. 1, then using cylindrical coordinates the geometry is reduced to a longitudinal r - z plane, obtained by assuming the adsorption column to be axisymmetric. Geometrical dimensions and operational parameters are shown in Table 1, whereas Tables 2 and 3 provide, respectively, the physical properties of the material and the mass transport parameters, including the kinetics of the adsorption process. These experimental data were obtained or

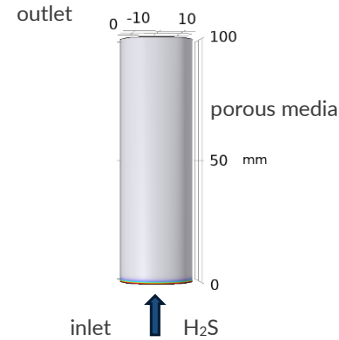


Figure 1. Schematic of the porous fixed-bed column.

Table 1. Geometrical dimensions and operational parameters of the porous bed-fixed reactor.

Magnitude	Value
Length L of the fixed-bed reactor	100 mm
Inner diameter D of the reactor	30 mm
Volume V of the reactor	$7.0686 \times 10^{-5} \text{ m}^3$
Gas flow rate Q	$1.833 \times 10^{-5} \text{ m}^3/\text{s}$
Molar concentration of gas inflow $C_{o \text{ gas}}$	40.876 mol/m^3
Molar concentration of H ₂ S inflow $C_{o \text{ H2S}}$	0.08094 mol/m^3

Table 2. Physical properties of the materials.

Magnitude	Value
Gas density ρ_{gas}	1.1012 kg/m^3
Gas dynamic viscosity μ_{gas}	$1.32 \times 10^{-5} \text{ Pa}\cdot\text{s}$
Bed density ρ_b	481 kg/m^3
Pellet density ρ_s	2505.4 kg/m^3
Bed porosity ϵ_b	0.80801
Pellet porosity ϵ_s	0.21
Pellet diameter d	0.002 m
Mass of pellets in the bed m_{ads}	0.034 kg
Surface area of a pellet by BET S_{bet}	$89937 \text{ m}^2/\text{kg}$
Total surface area of all pellets per bed volume S_{area}	$4.326 \times 10^7 \text{ 1/m}$
Tortuosity factor of the porous bed τ	3

Table 3. Mass transport parameters.

Magnitude	Value
Molecular diffusivity of H ₂ S in the CH ₄ +CO ₂ gas D_F	$0.16 \text{ cm}^2/\text{s}$
Axial dispersion coefficient D_z	$5.4 \times 10^{-4} \text{ m}^2/\text{s}$
Langmuir constant KL	31.72 mol/m^3
Langmuir adsorption maximum C_{pLmax_ads}	0.35 mol/kg
Freundlich constant KF	0.1039 mol/kg
Freundlich exponent n_F	0.6063
External mass transfer coefficient k_g	0.037874 m/s
Overall mass transfer coefficient h_{LDF}	0.00789 1/s

computed from the work of Aguilera and Gutierrez [6].

2.2. Governing equations

In COMSOL Multiphysics®, we describe the gas flow using the Brinkman Equations interface for porous media, whereas the Transport of Diluted Species in Porous Catalysts interface accounts for the evolution of the species by diffusion, convection and mass transfer mechanisms [14]. For the adsorption process, the mass transfer in the fluid inside the porous matrix is treated by means of a Linear Driving Force (LDF) model [14, 15]. On the other hand, the adsorption of H₂S onto the porous particles is modeled using the nonlinear Langmuir isotherm in one case and the Freundlich isotherm in the other. Assuming the gas flow is weakly compressible, the velocity distribution in the porous domain is determined by solving the steady-state conservation of linear momentum and the continuity equation

$$\frac{\rho}{\varepsilon_b} (\mathbf{u} \cdot \nabla) = -\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_b} \left\{ \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T - \frac{2\mu}{3} (\nabla \cdot \mathbf{u}) \mathbf{I}) \right\} - \left[\kappa^{-1} \mu + \rho \beta |\mathbf{u}| + \frac{Q_m}{\varepsilon_b^2} \right] \mathbf{u} + \mathbf{F} \right] \quad (1)$$

$$\nabla \cdot (\rho \mathbf{u}) = Q_m \quad (2)$$

where ρ is the density (kg/m³), $\mathbf{u}$ (m/s) the velocity, p (Pa) the pressure, μ (Pa·s) the dynamic viscosity (Pa·s), $\mathbf{I}$ means the identity tensor, $\mathbf{F}$ are the volume external forces applied to the fluid (N/m³), and t (s) is the time. For the porous medium, ε_b is the bed porosity, κ (m²) the permeability, and Q_m (kg/(m³·s)) a mass source or sink. The magnitude $-\rho \beta |\mathbf{u}| \mathbf{u}$ represents the viscous Forchheimer drag force and β is a parameter dependent on the porous medium permeability.

The transport of diluted H₂S in the solvent gas of the porous fixed-bed reactor is governed by convection and diffusion mechanisms, the latter described by Fick's law. In this case, the conservative formulation of the species conservation in a saturated porous medium is

$$\frac{\partial(\varepsilon_b c)}{\partial t} + \frac{\partial(\rho_b c_p)}{\partial t} + \nabla \cdot (\mathbf{J} + \mathbf{u}c) = R + S + R_{ads} \quad (3)$$

where c is the molar concentration (mol/m³) of H₂S in the solvent gas, c_p the amount adsorbed onto the solid particles (mol/kg of solid), ρ_b the solid bulk density corresponding to the density of the bed (kg of solid/m³), $\mathbf{J}$ the diffusive mass flux vector (mol/(m³·s)), R (mol/(m³·s)) a reaction rate of the reactions in the porous bed, S (mol/(m³·s)) an arbitrary source/sink term, and R_{ads} (mol/(m³·s)) the overall adsorption rate accounting for the adsorption process in the porous medium.

The diffusive mass flux vector $\mathbf{J}$ is defined as

$$\mathbf{J} = -(D_D + D_e) \nabla c \quad (4)$$

where D_D and D_e are given in (m²/s) and represent respectively, the dispersion diffusivity (mechanical mixing) of the medium and the effective diffusivity of H₂S. We neglect the dispersion diffusivity and use the tortuosity model to describe the effective diffusivity (the Brownian motion is impeded by the grains) as

$$D_e = \frac{\varepsilon_b}{\tau} D_F \quad (5)$$

where D_F (m²/s) is the molecular diffusivity of H₂S in the gas mixture, which can be determined using the Chapman-Enskog theory [1,7,8] or by the Fuller-Schetter-Gridding correlation [6,11].

The term R_{ads} of Eq. 3 implemented in COMSOL Multiphysics® through the LDF model [14,15] is expressed by

$$R_{ads} = h_{LDF} (c_{ads} S_{area} - c_{e,p} \rho_b) \quad (6)$$

In Eq. 6 h_{LDF} (1/s) is the overall effective mass transfer coefficient (which includes both the external and internal mass transfer), c_{ads} (mol/m²) the local value of the adsorbed H₂S concentration, S_{area} (m²/m³) the specific area available for the adsorption, and $c_{e,p}$ (mol/kg) the equilibrium value of H₂S adsorbed per dry mass of adsorbent. It should be noted that ρ_b (kg of solid/m³), the bulk density of the bed, which is defined as mass of porous bed/volume of porous bed, equates to mass of solid/volume of porous bed. The value of h_{LDF} can be computed [5,6,15] by the equation

$$\frac{1}{h_{LDF} k_e} = \frac{d}{6 k_g} + \frac{d^2}{60 D_{e,p}} \quad (7)$$

where d (m), k_e (dimensionless), k_g (m/s), and $D_{e,p}$ (m²/s) are respectively, the solid particle diameter, the adsorption equilibrium constant, the external (film) mass transfer and the effective diffusivity of H₂S in the macropore (internal mass transfer).

Eq. 7 enables the computation of a global mass resistance for systems in which more than one mass transfer resistance is significant [15].

Finally, the magnitude $D_{e,p}$ of Eq. 7 can be evaluated by the Bosanquet approximation [5,16,17].

$$D_{e,p} = \frac{\varepsilon_s}{\tau} \left[\frac{1}{D_F} + \frac{1}{D_K} \right]^{-1} \quad (8)$$

where ε_s is the pellet porosity, D_F the former molecular diffusivity of H₂S for the molecule-molecule interactions, and D_K (m²/s) the Knudsen diffusivity for the H₂S molecule-wall interactions.

2.3. Equilibrium adsorption isotherms

To compute the equilibrium adsorption value ($c_{e,p}$) of H_2S , we use two different non-linear models, the Langmuir isotherm and the Freundlich isotherm [3,15], which were also set up in the work of Aguilera and Gutierrez [6] to fit their experimental data. In COMSOL Multiphysics®, we define, respectively, the Langmuir constant (KL) and the Langmuir adsorption maximum (c_{pLmax_ads}) for the first isotherm

$$c_{e,p} = \frac{KL (c_{pLmax_ads}) c}{1 + (KL) c} \quad (9)$$

and the Freundlich constant KF and the Freundlich exponent n_F for the second one

$$c_{e,p} = KF \left[\frac{c}{c_{ref}} \right]^{n_F} \quad (10)$$

where c_{ref} is a reference value of 1 mol/kg.

2.4. Initial and boundary conditions

The following initial and boundary conditions are fixed to obtain the computational solution of the governing partial differential equations, describing H_2S adsorption from biogas.

- Brinkmann equations

A gas flowrate of $1.833 \times 10^{-5} \text{ m}^3/\text{s}$ is set at the inlet for a mixture of methane (60% vol.), hydrogen sulfide (1980 ppm) and carbon dioxide (balance), for all time. Moreover, we use a condition of no slip for the gas flow on the solid walls, a symmetry condition for the central longitudinal z axis of the porous reactor, and a relative pressure equal to zero at the outlet.

- Transport of diluted H_2S in the porous reactor

The molar concentration of H_2S is fixed in the gas inflow, according to Table 1, whereas a dominant convective mass transport is assumed on the outflow, neglecting diffusive mechanisms at the exit of the reactor. Axial symmetry is used for the central longitudinal z axis of the porous reactor and conditions of no mass flux are set on the solid walls. Finally, the initial concentration of H_2S in the reactor is equal to zero.

2.5. Solution with COMSOL Multiphysics®

The numerical solution of the differential equations of the model is obtained by dividing the study into two steps. The first stationary study step solves the pressure and velocity from the Brinkmann Equations interface, whereas a subsequent time-

dependent study computes the mass transfer magnitudes for the Transport of Diluted Species in Porous Catalysts interface. In this case, the Porous Catalyst node accounts for the evolution of the species by diffusion, convection and mass transfer mechanisms, including the adsorption process modeled by the equilibrium isotherms of Langmuir and Freundlich. The coupling between the physics of the Brinkman Equations and Transport of Diluted Species in Porous Catalysts interfaces is established by using the Reacting Flow, Diluted Species feature, synchronizing their relationship. The meshing strategy uses a structured quadrilateral mapped mesh, for which the maximum element size is 0.2 mm and the minimum element size is 3×10^{-4} mm. Also, 12 boundary layers are created on the solid walls using default values of the software. Finally, the number of degrees of freedom (DOFs) to be solved for is 218088 plus 44678 internal DOFs, both for the Langmuir and Freundlich adsorption models.

3. Results and Discussion

For the adsorption process described by the Langmuir isotherm, Fig. 2 shows the concentration profile of H_2S along the length of the porous reactor at six different times, separated by a constant interval of 20 min. We observe that mass transfer begins immediately upon introduction of the gas in the column, causing the adsorbate concentration to decrease along the length z of the bed, until it reaches nearly zero. For the same case, Fig. 3 illustrates the concentration values of H_2S

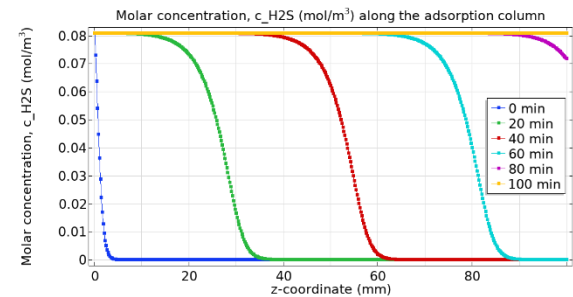


Figure 2. Molar concentration profile of H_2S along the adsorption column, using the Langmuir isotherm.

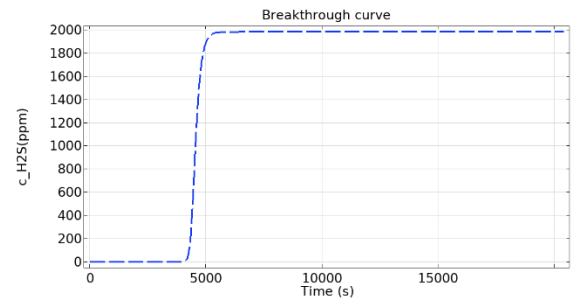


Figure 3. Breakthrough curve, using the Langmuir isotherm.

in the outflow ($z=L$), which allows for the computation of the breakthrough time, i.e. when the adsorbate starts to leave the column [3].

Also, we observe that, approximately after 5000 s, the concentration of H_2S in the effluent is equal to the inflow concentration of 1980 ppm.

Figs. 4 and 5 refer to the adsorption process described by the Freundlich isotherm and plot the H_2S concentration profile along the coordinate z and the breakthrough curve, respectively. The mass transfer zone (MTZ) of Fig. 4, which is represented by the length over which the concentration changes [3], is larger than the MTZ of Fig. 3, computed for the Langmuir isotherm. Analogously, the breakthrough curve of Fig. 5 is different from the corresponding curve plotted in Fig. 4 and, to reach the inflow concentration of H_2S , a time greater than 5000 s is required. Furthermore, the predicted breakthrough curve obtained with the Freundlich isotherm highlights a rounded shape in the final section of the curve. This behavior was also observed by Aguilera and Gutierrez [6], who compared their numerical results with experimental measurements and concluded that the Freundlich model was more realistic.

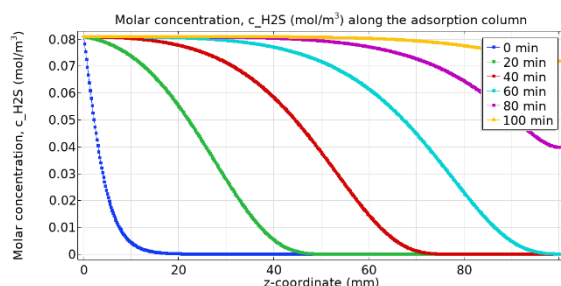


Figure 4. Molar concentration profile of H_2S along the adsorption column, using the Freundlich isotherm.

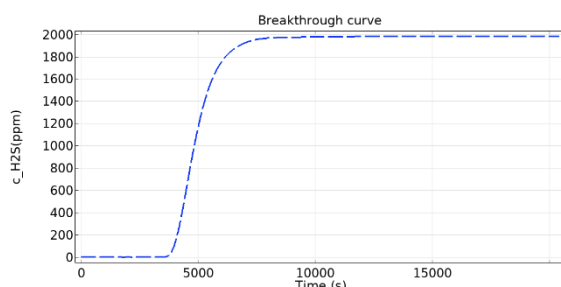


Figure 5. Breakthrough curve, using the Freundlich isotherm.

4. Conclusions

The computational results describe satisfactorily the adsorption process of H_2S from biogas, showing the influence of the main operational parameters. The evolution of the mass transfer zone in the porous fixed-bed column is also well characterized, showing its progression along the length of the

reactor. The breakthrough curves simulated by the model indicate favorable kinetics and bed efficiencies.

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