

Pressure Swing Adsorption Technology Using 5A Zeolite for the Removal of H₂S in the Fixed Bed Reactor

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Proposed model for H₂S was analyzed using a stationary adsorbent bed allowing continuous operation. The numerical method of inverse Laplace transform was used to solve the one-dimensional isothermal mathematical model that describes the process. For the simulation, a computer code in Fortran 90 language was developed to solve the problem in dynamic regime. The objective of this research has been to formulate a robust mathematical model for the adsorption process of H₂S on nanostructured solid (NaX) at 25 °C and pressures at 1.01 bar. The adsorption capacity of catalytic adsorbent using H₂S has been analyzed as well as the simulation of H₂S in liquid and solid phases for different initial superficial velocities.

1. Introduction

The hydrogen sulfide (H₂S) is a toxic gas, highly corrosive, harmful to the human health and to the environment, being associated with the formation of acid rain and the greenhouse effect. This component (H₂S) can damage equipment and oil pipelines. Thus, levels of H₂S in heavy oil out of allowed by security standards may represent an increase in logistics and maintenance costs of a petrochemical industry. Aiming the importance of controlling the levels of H₂S, this research was proposed to study the adsorption process for removal of H₂S in heavy oil in a fixed bed reactor using a mathematical model.

Various problems in engineering, mathematical physics, theoretical physics, chemical physics and theoretical biology are modelled by the so-called initial value and boundary problems. In the last three decades, numerous works have been focused on the development of more advanced and efficient methods for stiff problems. The situation becomes more complicated when stiffness is coupled with nonlinearity. Recently, the inverse Laplace transform method (ILTM) has been used to solve these type problems (linear and nonlinear) as well as the hybrid Laplace transform method (HLTM). The main advantage of these methods is to solve both linear and nonlinear equations without linearization (Silva and Abreu, 2012).

Many transform methods often require complicated techniques to overcome mathematic difficulties for nonlinear transient problems (Sheng et al., 2011). Boundary value problems have been solved using the ILTM (Jin et al., 2003). These authors studied a mathematical model in slurry bubble systems. The Laplace transform is also very suitable to combine with other numerical techniques. Ahn et al. (2010) studied the hybrid method for solving the Black-Scholes equation. The hybrid method has been used to transform the proposed mathematical model from the time domain into the spectrum domain followed by use of the finite difference or finite element methods. This method does not consume very computer time when applying to nonlinear equations (Chen et al., 2006).

The present paper aims at applying the ILTM for solving the adsorption process of H₂S in a catalytic three-phase fixed bed reactor with catalytic particles of nanopores. Moreover, the solving algorithm was validated using literature data.

2. Mathematical modelling

2.1 Process detail

The process studied in this work consists in the chemical transport of H₂S in catalytic three-phase fixed bed reactor with stationary catalytic adsorbent (NaX). The adsorption dynamics of this process is the development of mobile H₂S (concurrent-downward) over the stationary adsorbent phase. A one-dimensional mathematical model has been developed for H₂S for analyzing the adsorption process. The adsorbent pellets were of spherical shape of 0.156 cm diameter and 0.748 ncm nanopores.

2.2 Governing equations

The proposed mathematical model was described by a partial differential equation system and it is restricted to the following assumptions: (i) isothermal system; (ii) all flow rates are constant throughout the reactor; (iii) the intraparticle diffusion resistance was considered; (iv) no radial concentration gradient. Based on the above assumptions, axial mass balance equation of H₂S could be written as follows.

$$\frac{\partial C_{H_2S}(z,t)}{\partial t} + V_{sg} \frac{\partial C_{H_2S}(z,t)}{\partial z} = D_{ax} \frac{\partial^2 C_{H_2S}(z,t)}{\partial z^2} - \frac{k_s a_s}{\epsilon_{ex}} [C_{H_2S}(z,t) - C_s(r,t)]_{r=R} \quad (1)$$

The initial and boundary conditions for the Eq(1) are given as follows:

$$C_{H_2S}(z,t)|_{t=0} = C_{H_2S,0}; \text{ for } 0 \leq z \leq L \quad (2)$$

$$\frac{\partial C_{H_2S}(z,t)}{\partial z} \Big|_{z=0^+} = \frac{V_{sg}}{D_{ax}} [C_{H_2S}(z,t)|_{z=0^+} - C_{H_2S}(t)]; \text{ for } t \geq 0 \quad (3)$$

$$\frac{\partial C_{H_2S}(z,t)}{\partial z} \Big|_{z=L} = 0; \text{ for } t \geq 0 \quad (4)$$

The mathematical model developed to describe the intraparticle diffusional mass transfer (IDMT) of H₂S in the adsorbent has been considered. It is important to note that IDMT involves two different phenomena such as micropore diffusion (the adsorbate first diffuses in the gas filling the nanopores and then is adsorbed) and surface diffusion (the adsorbate is first adsorbed then diffuses from one site to another). Based on these two assumptions, the intraparticle diffusional mass balance of H₂S is given as:

$$\epsilon_s \frac{\partial C_s(r,t)}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_s(r,t)}{\partial r} \right] + \rho_s \frac{\partial q(r,t)}{\partial t} + \rho_s k_r q(r,t) \quad (5)$$

The initial and boundary conditions for the Eq(5) are presented as:

$$C_s(r,t)|_{t=0} = 0; \text{ for } 0 \leq r \leq R \quad (6)$$

$$D_s \frac{\partial C_s(r,t)}{\partial r} \Big|_{r=R} = k_s [C_{H_2S}(z,t) - C_s(r,t)]_{r=R}; \text{ for } t \geq 0 \quad (7)$$

$$\frac{\partial C_s(r,t)}{\partial r} \Big|_{r=0} = 0; \text{ for } t \geq 0 \quad (8)$$

Reversible adsorption occurs at the sites (σ) into an adsorbent particle according to first step mechanism below.



Based on this first-step mechanism, the adsorption rate of H₂S can be written as follows:

$$\frac{\partial q(r,t)}{\partial t} = k_a \left[C_s(r,t) - \frac{q(r,t)}{K} \right] - k_r q(r,t) \quad (10)$$

The initial condition for the Eq(10) has been described as:

$$q(r,t) \Big|_{t=0} = 0; \text{ for } 0 \leq r \leq R \quad (11)$$

2.3 Solution in the Laplace domain

Laplace transforms are powerful tools used primarily for solving differential equations. The principal difficulty in using them is finding their inverses. The mathematical model given here by PDEs (1) to (11) and their initial and boundary conditions were easily transformed using the Laplace transformation according to transformed Eq(12) as follows.

$$\bar{C}_i(z,s) = \int_0^{\infty} C_i(z,t) e^{-st} dt; \bar{C}_i(z,s) = \bar{C}_{H_2S}(z,s), \bar{C}_s(r,s) \text{ and } \bar{q}(r,s) \quad (12)$$

Eq(1) to Eq(11) and their initial and boundary conditions were obtained in the Laplace domain using the above Eq(12) as follows.

Mass balance for H₂S (gas phase) in the Laplace domain:

$$\frac{d^2 \bar{C}_{H_2S}(z,s)}{dz^2} - \alpha_1 \frac{d \bar{C}_{H_2S}(z,s)}{dz} - \alpha_2(s) \bar{C}_{H_2S}(z,s) + \alpha_3 \bar{C}_s(R,s) = -\frac{C_{H_2S,0}}{s D_{ax}} \quad (13)$$

The initial and boundary conditions of H₂S in the Laplace domain:

$$\bar{C}_{H_2S}(z,s) \Big|_{z=0} = \frac{C_{H_2S,0}}{s}; \text{ for } 0 \leq z \leq L \quad (14)$$

$$\frac{d \bar{C}_{H_2S}(z,s)}{dz} \Big|_{z=0^+} = \frac{V_{sg}}{D_{ax}} \left[\bar{C}_{H_2S}(z,s) \Big|_{z=0^+} - \bar{C}_{H_2S}(s) \right]; \text{ for } s \geq 0 \quad (15)$$

$$\frac{d \bar{C}_{H_2S}(z,s)}{dz} \Big|_{z=L} = 0; \text{ for } s \geq 0 \quad (16)$$

Mass balance for H₂S (solid phase) in the Laplace domain:

$$\frac{d^2 \bar{C}_s(r,s)}{dr^2} + \frac{2}{r} \frac{d \bar{C}_s(r,s)}{dr} - \beta_5(s) \bar{C}_s(r,s) = 0 \quad (17)$$

The initial and boundary conditions of H₂S in the Laplace domain:

$$\bar{C}_s(r,s) \Big|_{s=0} = 0; \text{ for } 0 < r \leq R \quad (18)$$

$$\frac{d \bar{C}_s(r,s)}{dr} \Big|_{r=R} = \frac{k_s}{D_s} \left[\bar{C}_f(z,s) - \bar{C}_s(r,s) \Big|_{r=R} \right]; \text{ for } s \geq 0 \quad (19)$$

$$\frac{d \bar{C}_s(r,s)}{dr} \Big|_{r=0} = 0; \text{ for } s \geq 0 \quad (20)$$

The adsorption rate of H₂S in the Laplace domain:

$$\bar{q}(r,s) = \alpha_5(s) \bar{C}_s(r,s) \quad (21)$$

The initial condition in the Laplace domain for the Eq(21) has been described as:

$$\bar{q}(r, s) \Big|_{s=0} = 0; \text{ for } 0 \leq r \leq R \quad (22)$$

The coefficients [α_1 , $\alpha_2(s)$, α_3 , $\alpha_5(s)$ and $\beta_5(s)$] of Eq(13), Eq(17) and Eq(21) are defined in the appendix (A). The general solution of the concentration of H₂S in the gas phase:

$$\bar{C}_{H_2S}(z, s) = \exp(\eta_1 z) \left\{ \frac{\omega_3(s)}{\omega_2(s)} \cosh[\eta_2(s)z] + \frac{\omega_3(s)}{\omega_4(s)} \sinh[\eta_2(s)z] \right\} + \frac{C_{H_2S,0}}{\omega_1(s)sD_{ax}} \quad (23)$$

2.4 Numerical inversion of Laplace transform

The numerical inversion of Laplace transform was used to obtain the concentration of H₂S in the gas phase at the exit of fixed bed reactor. Using the trapezoidal rule, the approximation for the numerical inversion of the Eq(23) can be described as follows.

$$C_{H_2S}(t) \approx \frac{\exp(\gamma)}{T} \left\{ \frac{\bar{C}_{H_2S}(s_0)}{2} + \sum_{k=1}^{\infty} \text{Re}[\bar{C}_{H_2S}(s_k)] \exp\left(\frac{ik\pi}{T}\right) \right\} \quad (24)$$

Where,

$$s_k = \gamma + \frac{ik\pi}{T}; k = 0, 1, 2, \dots; 0 < t < 2T. \quad (25)$$

3. Results and discussions

The mathematical modelling has been developed to analyze the behaviour of H₂S within the catalytic three-phase fixed bed reactor. Numerical experiments were performed at the exit of fixed bed to H₂S. Parameters for feeding the computational code are shown in Table 1. In this Table, the operating conditions, gas and solid properties are presented.

Table 1: Input values of operating conditions, properties of the gas and solid phases used in the simulation

Categories	Properties	Numerical Values
Operation Conditions	Operation temperature of the gas phase, T _g , K	298
	Operation pressure, p _{op} , bar	1.01
	Initial superficial velocity, V _{sg,0} , m/s	5.47x10 ⁻² - 2.67x10 ⁻²
	Initial concentration of H ₂ S in the gaseous phase, C _{H₂S,0} , mol/m ³	0.12
	Initial concentration of H ₂ S in the nanopores space of solid particles, C _{H₂S,0} , mol/m ³	0.00
	Initial adsorbed concentration of H ₂ S on the solid particles, q _{H₂S,0} , mol/m ³	0.00
	Reaction constant, k _r , 1/s	0.2
Gas properties	Dispersion coefficient of H ₂ S, D _{ax} , m ² /s	1.43x10 ⁻²
	Gas-solid mass transfer coefficient, k _s , m/s	2.53x10 ⁻³
	Effective diffusivity coefficient of H ₂ S, D _s , m ² /s	3.19x10 ⁻³
	Adsorption rate coefficient, k _a , 1/s	2.31x10 ⁻²
	Adsorption equilibrium coefficient, K, m ³ /mol	0.672
	External void fraction, ε _{ex}	0.39
Properties of the solid phase	Density of the solid phase, ρ _s , kg/m ³	1.125x10 ³
	External area of particles per unit volume of reactor, a _s , m ⁻¹	156.45
	Solid porosity, ε _s	0.59

The Figure 1 shows a validation of the solving algorithm by comparing to the predicted concentrations (adsorbed) of H₂S obtained using one Initial superficial velocity. Experimental databases have been employed in the model adjustment. The adjustment has been confirmed a good validation between an experimental databases of H₂S and the model equation presented by the Eq(24), where parameter values were expressed in Table 1 as follows.

Figures (2a) and (2b) show the simulations of the concentrations in gas and solid phases of H₂S obtained at the exit of the catalytic trickle-bed reactor for four different initial superficial velocities. In particular, Figure (2a)

is a plot of the concentration of H₂S in gas phase versus time. On the other hand, Figure (2b) is a plot of the concentration of H₂S in solid phase versus time.

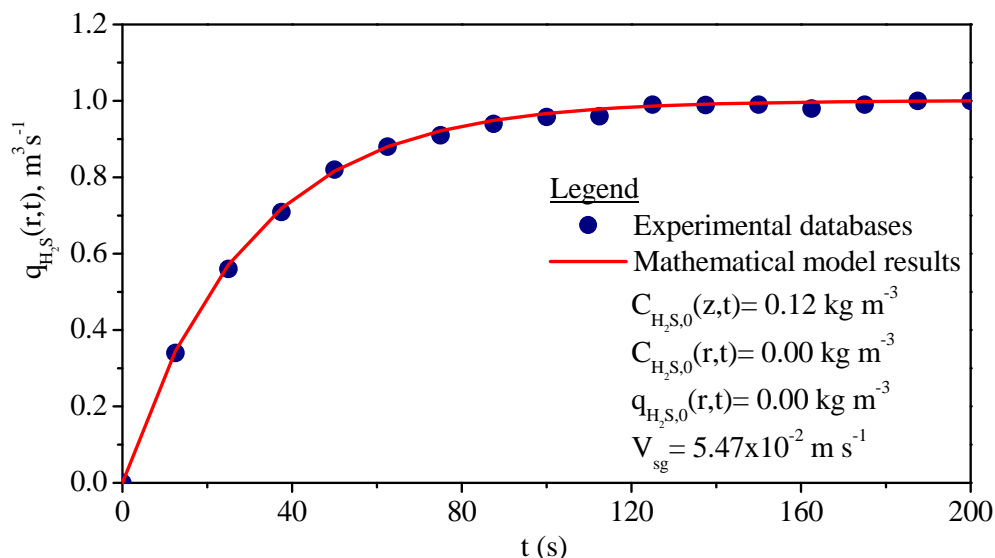


Figure 1: Comparison between experimental databases of H₂S (adsorbed) obtained at the exit of the catalytic trickle-bed reactor for one different initial superficial velocity of gas.

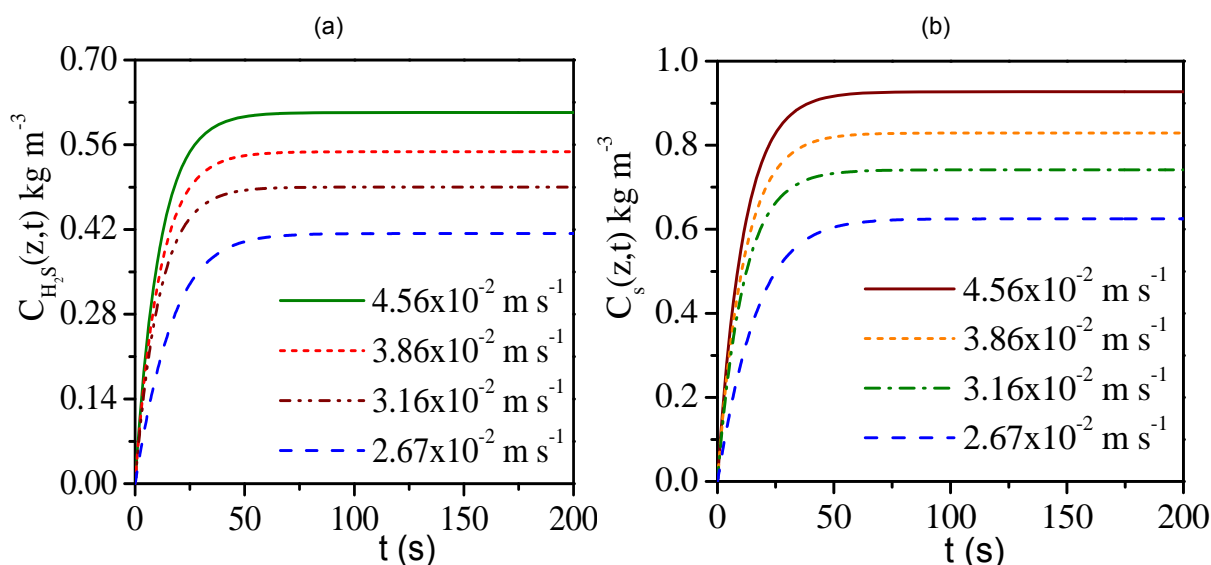


Figure 2: Simulations for the concentrations in gas and solid phases of H₂S obtained at the exit of the catalytic trickle-bed reactor for four different initial superficial velocities of gas.

4. Conclusions

Catalytic trickle-bed system of fixed bed (N₂/H₂O-H₂S/ NaX) was evaluated using an experimental dynamic method and via predictions of a phenomenological mathematical model. Operating at 298 K under 1.01 bar with solid and gas phases flowing under constant initial superficial velocity of liquid ($V_{sl} = 6.17 \times 10^{-3} \text{ m s}^{-1}$) and initial superficial velocity of gas varying in the range from $5.47 \times 10^{-2} \text{ m s}^{-1}$ to $2.67 \times 10^{-2} \text{ m s}^{-1}$. The magnitudes of concentrations increase according to the growth of initial superficial velocities of gas as Figures (2a) and (2b) has shown. Based on the values of the parameters presented in Table 1, the model was validated by comparing using experimental data bases with a mean relative error of 2.54%.

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Appendix A

$$\alpha_1 = \frac{V_{sg}}{D_{ax}} \quad (\text{A1})$$

$$\alpha_2(s) = \frac{1}{D_{ax}} \left(s + \frac{k_s a_s}{\varepsilon_{ex}} \right) \quad (\text{A2})$$

$$\alpha_3 = \frac{k_s a_s}{\varepsilon_{ex} D_{ax}} \quad (\text{A3})$$

$$\alpha_5(s) = \frac{k_a}{\left(s + k_r + \frac{k_a}{k} \right)} \quad (\text{A4})$$

$$\beta_5(s) = \left(\frac{\varepsilon_s s}{D_s} - \frac{(\rho_s s + \rho_s k_r)}{D_s} \frac{k_a}{\left(s + k_r + \frac{k_a}{k} \right)} \right) \quad (\text{A5})$$

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